REACTIONS OF C_3-HYDROCARBONS ON Pt/ALUMINA AND CHROMIA/ALUMINA CATALYSTS

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by

Isobel M Matheson

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SUMMARY

The deactivation phenomena associated with the interaction of alkanes and alkynes with platinum and chromia catalysts has been investigated with a view to establishing conditions under which transhydrogenation could be effected. ^{2}H- and ^{13}C-stable isotope techniques were used to (a) establish the origins and fates of the carbon and hydrogen during the reactions and (b) obtain a detailed understanding of the reaction mechanisms, including the coking process.

When propane or propyne or a 1:1 mixture of propane and propyne was passed over a Pt/alumina catalyst, in the temperature range 500°C - 600°C, it was found that the main reaction taking place was dissociation of the hydrocarbons and subsequent formation of a carbonaceous overlayer on the catalyst. Isotopic tracer studies revealed that, within the carbonaceous deposit, there was considerable mixing of both carbon and hydrogen.

When unlabelled and perdeutero propane were passed over chromia/K/alumina, in the temperature range 500°C to 600°C, a significant hydrogen-deuterium isotope effect was observed. At 500°C this isotope effect was large enough to prevent dehydrogenation of perdeutero propane. Though still present at 550°C and 600°C, the isotope effect was less significant.

The rate determining step of propane dehydrogenation on

chromia/K/alumina was found to be

$$C_3H_8 \text{ (ads)} \rightarrow C_3H_6 \text{ (ads)} + H_2 \text{ (ads)}.$$

From results of experiments investigating the interaction of propane with chromia/K/alumina, a sequential model for dehydrogenation of propane was devised.

During the interaction of propyne with chromia/K/alumina, in the temperature range 500°C to 600°C, the main reaction which took place was found to be dissociation of propyne. When a 1:1 mixture of propane and propyne was passed over chromia/K/alumina, in the temperature range 500°C to 600°C, transhydrogenation did in fact take place.

The three types of reaction observed to occur on chromia/K/alumina, dehydrogenation, hydrogenation and transhydrogenation, were accompanied by some dissociation of the relevant hydrocarbon. This resulted in the formation of a carbonaceous overlayer on the surface of the catalyst. Again isotopic tracer techniques revealed that there was considerable isotopic mixing on the surface of the catalyst.

On both platinum/alumina and chromia/K/alumina the amount of carbon which could be removed from the used catalyst, by high temperature treatment with dioxygen, was found to be dependent on the ratio of total carbon to total hydrogen lost to the catalyst during a

reaction. The more hydrogen deficient was the carbonaceous overlayer the easier it was to remove carbon.

It was concluded that, in terms of these results, chromia/K/alumina exhibits greater transhydrogenation activity than platinum/alumina.

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Chapter ONE

INTRODUCTION

1.1 TRANSHYDROGENATION

At the present time there is much interest in developing a more economical process for the production of alkenes. There are three possible methods which produce alkenes from alkanes:-

1. DEHYDROGENATION - which involves removal of hydrogen over a suitable catalyst.

$$\text{e.g. } C_4H_{10} \rightarrow C_4H_8 + H_2$$

2. OXIDATIVE DEHYDROGENATION - which involves dehydrogenation with oxygen containing species present. Good yields are obtainable at lower temperatures than in direct dehydrogenation.

$$\text{e.g. } 3\ C_3H_8 + SO_2 \rightarrow 3\ C_3H_6 + H_2S + 2\ H_2O$$

3. TRANSHYDROGENATION - which involves the transfer of hydrogen between two molecules, and therefore requires a suitable receptor.

$$\text{e.g. } C_3H_8 + C_4H_6 \rightarrow C_3H_6 + C_4H_8$$

Catalysts and systems capable of performing options (1) and (2) are known.[1,2] However, option (3) is, in principle, a less demanding reaction than options (1) or (2) and there is therefore a considerable commercial incentive in developing the process.

As can be seen from the above example, an alkyne or a diene is a suitable receptor for transhydrogenation. They have the added

advantage that by accepting hydrogen they produce a further mole of alkene.

As it is impossible to look at all transhydrogenation reactions the reaction between propane and propyne has been chosen for this investigation.

$$\text{PROPANE} + \text{PROPYNE} \rightarrow 2\ \text{PROPENE}$$

$$C_3H_8 + C_3H_4 \rightarrow 2C_3H_6$$

As well as being representative of transhydrogenation, by virtue of its simplicity, this reaction provides various experimental advantages.

Clearly, for transhydrogenation to occur, it must be possible to (a) dehydrogenate the alkane, and (b) hydrogenate the alkyne or diene, under similar experimental conditions.

Dehydrogenation reactions are endothermic and thermodynamically limited. For propane, the enthalpy of dehydrogenation is 126.0 kJ mol^{-1}.[3]

$$C_3H_8 \rightarrow C_3H_6 + H_2 \qquad \Delta H^0 = +126.0\ \text{kJ mol}^{-1}$$

For favourable equilibrium, without a catalyst present, temperatures in excess of 1000°C are required. As the number of moles increases on dehydrogenation, improved conversion at equilibrium is obtained by operation at as low a partial pressure of hydrocarbon as feasible. For maximum selectivity contact times of a fraction of a

second are preferred.

On the other hand, hydrogenation reactions are exothermic. For propyne, the enthalpy of hydrogenation is -291.6 kJ mol^{-1}.[3]

$$C_3H_4 + H_2 \rightarrow C_3H_6 \quad \Delta H^0 = -291.6 \text{ kJ mol}^{-1}$$

It has been found that, for hydrogenation of alkynes, reaction rate reaches a maximum at temperatures between 180 and 200°C,[4] above which the rate falls with increasing temperature.

Clearly, the thermodynamic differences in dehydrogenation and hydrogenation reactions are going to be a major factor in transhydrogenation processes. Thermodynamically, dehydrogenation requires high temperatures to achieve measurable equilibrium yields of alkene. However, the use of such high temperatures results in extensive dissociation of the hydrocarbon and consequential coking of the catalyst surface. A problem which is more acute with unsaturated hydrocarbons than with alkanes.

The concept of catalyst coking, or formation of a carbonaceous overlayer on a catalyst, during reactions of hydrocarbons with metal surfaces was referenced by Sabatier *et al.*[5] in 1902. During the hydrogenation of ethene these workers noted that a surface carbonaceous deposit, which had detrimental effects on catalytic behaviour, was formed. Similarly, Beeck[6] made reference to the formation of a surface

carbonaceous deposit, which poisoned the catalyst surface, during the interaction of hydrocarbons with metal films.

Recently, investigations have concentrated on the formation of carbonaceous deposits and on determining their role in catalytic behaviour of the surface, rather than acting only as a catalyst poison.

In a report on hydrogenation reactions, covering the period from 1970 to 1976, Webb[7] pointed out that there was a growing body of evidence to suggest that the hydrocarbon species that participates in the hydrogenation reaction is not adsorbed directly onto the metal, but is in fact adsorbed on a carbonaceous overlayer. Kesmodel *et al.*[8] have suggested that, during the adsorption of ethyne on Pt(III) surfaces, a carbonaceous overlayer is formed and hydrogenation is then from a second layer. Yasumori *et al.*[9, 10] have observed that, with polycrystalline palladium black catalysts, the preadsorption of ethyne produces a surface template effect for the polymerisation of ethyne to benzene and stabilises the activity of the catalyst for both ethene and ethyne hydrogenation.

Thomson and Webb[11] suggested a general mechanism for metal-catalysed hydrogenation of unsaturated hydrocarbons based on results from radiochemical studies. They proposed that, rather than interpreting such reactions as the addition of hydrogen to the adsorbed alkene, hydrogenation of unsaturated hydrocarbons should be interpreted as a

hydrogen transfer between an adsorbed hydrocarbon and the adsorbed alkene.

In his report Webb[7] also concluded that there was a growing body of evidence to suggest that not all carbon on a heterogeneous catalyst is deleterious. Somorjai[12] has suggested that only amorphous forms of carbon cause site blockage poisoning.

More recently Somorjai and Zaera[13] found that immediately after the start of a hydrocarbon reaction at atmospheric pressure, a carbonaceous layer was deposited on the catalyst surface and the reaction then occurred in the presence of this deposit. In fact, they found that a clean transition metal surface cannot readily catalyse hydrocarbon conversion reactions.

In a review of the formation of carbonaceous residues in metal-catalysed reactions of hydrocarbons Webb[14] found that the rate of formation of carbonaceous residues increases with:

(a) increasing temperature[15]

(b) decreasing total pressure[16]

(c) increasing hydrocarbon to hydrogen reactant ratio[17, 18]

(d) decreasing space velocity.[19]

Other factors which have an effect on the extent of carbonaceous deposit include, metal loading and metal dispersion of the catalyst, presence of surface chlorine or sulphur and the presence of a second

metal as a promoter. Webb[14] also noted that the commonly held view is that a promoter inhibits the formation of carbonaceous deposits.

Clearly, the role of carbonaceous deposits during the transhydrogenation process is of major importance to any investigation of transhydrogenation.

1.2 DEHYDROGENATION

The dehydrogenation process has long been of major importance to the petrochemical industry. A review of the development of the process and the catalysts it uses was carried out by Kearby in 1955.[20] Recent work has served to reinforce early findings and has tended to concentrate more on improvement of the catalysts, obtaining more detailed characterisation of the catalysts and on establishment of the mechanisms of reactions.

Between 1919 and 1932 early investigators of the dehydrogenation process considered catalysts such as nickel, platinum, palladium, iron, cobalt and copper.[21-25] These catalysts were found to be generally unstable and produced secondary cracking reactions. Investigations of catalytic dehydrogenation were greatly enhanced when Frey and Huppke studied the equilibrium of the dehydrogenation reaction and found the superior properties of chromia catalysts.[26]

Bergin *et al.*[27] found that activated alumina could be used for the

dehydrogenation of both propane and isobutane, giving initial yields of 32 to 36 % alkene at 650°C and 4560 v/v/hr. These workers also confirmed Beeck's[28] report that the addition of small amounts of water had a beneficial effect for dehydrogenation over activated alumina, although large amounts of water were found to inhibit the reaction.

When oxides of chromium, vanadium, iron, zinc or nickel were added to the activated alumina it was found that less severe dehydrogenation conditions were required. Of these alumina-supported catalysts it was found that chromia on alumina gave the best results. For example, excellent yields of propene from propane were found by Grosse and Ipatieff[29] using a chromia/alumina catalyst. Grosse[30] stated that the most favourable catalyst should contain less than 10 % chromia on alumina.

Chromia/alumina catalysts were widely used in commercial dehydrogenation processes. The Phillips dehydrogenation process[31], the Universal Oil Company dehydrogenation process[32] and the Houdry butane dehydrogenation process all used chromia/alumina catalysts in cyclic fixed bed reactors. In the butane dehydrogenation process used by the I. G. Farbenindustrie[33] the use of a chromia/alumina catalyst promoted with potassium was preferred.

In his review Kearby[20] concluded that, though many different dehydrogenation catalysts were reported in patent literature, judged by

actual use, chromia/alumina was the best catalyst for converting gaseous alkanes to alkenes.

More recently several groups have studied the active sites or phases in chromia/alumina dehydrogenation catalysts. Van Reijen *et al.*[34] studied the nature of the active sites of chromia, chromia/alumina and chromia/silica catalysts by magnetic susceptibility measurements, electron spin resonance, carbon monoxide and hydrogen chemisorption, gravimetry of the reduction treatment and rate measurement of the dehydrogenation of cyclohexane. These workers found that the conditions under which a chromia/alumina system becomes an active catalyst were those which favoured the presence of Cr^{2+} ions.

$$Cr^{3+}{}_2O_n + H_2 \rightleftharpoons Cr^{2+}{}_2O_{n-1} + H_2O$$

In the dehydrogenation reaction the rate determining step was found to be the dissociative chemisorption of the hydrocarbon, forming a metal-carbon and a surface hydroxyl bond.

Marcilly and Delmon[35] investigated the catalytic activity and stability to deactivation of a series of chromia-alumina solid solutions during the dehydrogenation of isobutane to isobutene. Solid solutions containing mainly chromia (chromia rich) were found to be most active in the early stages of the reaction. For solutions containing mainly alumina (alumina rich), α-phases were nearly inactive whereas γ-phases exhibited relatively high activities. Stability to deactivation decreased

from alumina rich to chromia rich solid solutions. Rather unexpectedly suggesting that the substitution of phases with a low content of chromia for the chromia rich phases detected in usual dehydrogenation catalysts would be beneficial. These workers conclude that the initial high activity of chromia rich solid solutions, which was rapidly inhibited, was probably due to the presence of Cr^{2+} ions. The useful dehydrogenation centres were the Cr^{3+} ions. They also concluded that the slow deactivation was initiated by ion pairs containing at least one Cr^{3+} ion. In alumina rich α solid solutions, substantially no surface Cr ions were present due to the strong covalent character of α-phases. The high activity of the γ-phases was attributed to the fact that γ-phases probably exhibit less covalent character.

Masson and Delmon[36] investigated the role of alkali metal and magnesium additives on the active phases in dehydrogenation catalysts. Potassium oxide, rubidium oxide and caesium oxide were found to increase the intrinsic activity and decrease the stability of the catalysts. Specific surface areas of the samples also increased. Their results suggested that the effective additives do not act directly through their basicity. They concluded that dehydrogenation and fouling were probably parallel reactions on identical Cr^{3+} active sites. Effective additives increased the Cr^{3+} active sites and inhibited recrystallisation to the α-phase.

Suzuki and Kaneko[37] investigated the dehydrogenation of propane over chromia/alumina/potassium oxide catalyst. They found the rate determining step of the reaction to be:-

$$C_3H_8\ (ads) \rightarrow C_3H_6\ (ads) + H_2\ (ads).$$

Recently De Rossi *et al.*[38, 39] have investigated propane dehydrogenation over chromia/zirconia[38], chromia/silica[39] and chromia/alumina.[39] Chromia/zirconia was found to exhibit the highest activity. These workers concluded that mononuclear Cr^{3+} with two coordinative vacancies was the active site for the dehydrogenation of propane.

Several groups have studied the use of platinum as a catalyst for the dehydrogenation of propane to propene. Biloen *et al.*[40] studied the rates of propane to propene dehydrogenation over platinum and very dilute platinum-in-gold alloys. These workers found that the rate per unit surface area of the alloy powders varied linearly with the bulk platinum concentration in the alloys. From this they concluded that only one platinum atom was involved in the rate determining step. They proposed that propane dehydrogenation over platinum and over the alloys occurs via the same reaction mechanism, namely, dissociative chemisorption of propane on a single platinum atom with which two adsorption sites are associated, one of which carries a hydrogen atom. The subsequent conversion of the propyl radical into π-bonded propene

via β-hydrogen elimination seemed to be the rate determining step. The last step, desorption of π-bonded propene, had a comparatively low activation energy.

More recently, Rennard and Freel[41] found platinum supported on magnesium aluminate spinel to be an efficient catalyst for high temperature, long cycle dehydrogenation of lower paraffins. These workers also found that trace amounts of sulphur in the feedstock (25 - 500 p.p.m.) suppressed both hydrogenolysis and coke formation.

1.3 HYDROGENATION

The metal-catalysed hydrogenation of unsaturated hydrocarbons has been the subject of a vast number of studies since the early work by Sabatier *et al.*[5] on the hydrogenation of ethene over metal catalysts. The Group VIII metals and copper, in the form of evaporated films, wires, foils powders or supported on a carrier such as alumina, silica or carbon, are most commonly used for these studies.

It is reasonable to assume that the chemisorption of an alkene or an alkyne precedes its hydrogenation and the nature of the adsorbed state has a direct bearing on the mechanism. It is generally accepted that the interaction of an unsaturated hydrocarbon with a metal surface results in both dissociative and associative chemisorption.[42] Studies have shown that, although it has been taken for granted that the associatively

adsorbed species is responsible for processes such as hydrogenation and isomerisation, dissociatively adsorbed species may also play an important part in processes such as alkene isomerisation[43, 44] and in alkene and alkyne hydrogenation.[11, 45, 46]

It has been widely accepted that in the hydrogenation of diunsaturated hydrocarbons the observed selectivity for alkene formation is a consequence of a thermodynamic factor, which controls the relative surface coverages of alkyne (or diene) and alkene, and a mechanistic factor, which determines the extent to which the alkene is further hydrogenated to alkane without undergoing intermediate desorption.[47-49] Such considerations infer the assumption that both alkyne and alkene adsorption and hydrogenation involve the same surface sites. However, a number of studies have suggested that this view is perhaps too simplistic and there is evidence to indicate that separate sites may be involved in the adsorption of alkyne and alkene under hydrogenation conditions.

From studies of the hydrogenation of ethyne in the presence of excess ethene over palladium/alumina catalyst, using (^{13}C)-ethyne as a tracer, Kemball *et al.*[50] have identified at least two distinct types of surface site. On type X sites the hydrogenation of both ethyne and ethene occurs, the ethyne being some 2200 times more strongly adsorbed than the ethene at 293 K (20°C). Type Y sites, which can be easily

poisoned by carbon monoxide, can hydrogenate ethene in the presence of ethyne, but are inactive for ethyne hydrogenation. Al-Ammar and Webb,[45, 51] reached similar conclusions from (^{14}C)-tracer studies of ethyne hydrogenation over supported palladium. rhodium and iridium catalysts. These workers showed that, under ethyne hydrogenation conditions, ethene was adsorbed to the same extent as in the absence of ethyne and they concluded that separate sites were involved. Addition of (^{14}C)- ethene to ethyne-hydrogen reaction mixtures showed that the ethene underwent hydrogenation independently of the hydrogenation of ethyne. Distinct sites for alkene and alkane formation have also been deduced from studies of propadiene hydrogenation over various silica-supported metals.[52]

Although there is a large amount of literature relating to alkyne hydrogenation most of it refers to the hydrogenation of ethyne. By comparison, the literature on the hydrogenation of propyne is relatively sparse. Bond and Sheridan[53] investigated propyne hydrogenation over pumice-supported nickel, palladium and platinum catalysts. These workers found that the reaction over nickel, palladium and platinum is largely simple hydrogenation, the early stages being principally a selective production of propene. However, small yields of reduced polymers of propyne were always also formed. A later study by Mann and Khulbe[54, 55] showed similar results. In the first stage of the reaction

the main product was propene. Later in the reaction the main process occurring was the further hydrogenation of propene to propane. These workers found pumice-supported palladium to be the most selective in propene formation.

Both these studies were carried out using static reactor systems monitoring pressure fall against time. More recently Jackson and Kelly[56] studied the hydrogenation of propyne over platinum/silica catalyst using a pulse-flow microreactor system. These workers found that as the temperature was raised, in the range 333 - 673 K (60 - 400°C), the activity of the catalysts increased. The rate of formation and yield of propene behaved similarly. At low temperatures carbon deposition had no discernable effect on propyne conversion or propene yield. At 473 K (200°C) the hydrocarbonaceous residue, formed from pulses containing equal amounts of hydrogen and propyne (i.e. 1:1 H_2:C_3H_4), acted as a catalyst poison and reduced the activity of the catalyst. As temperature was increased an increasing H_2:C_3H_4 ratio (from 1:1 to 3:1) was required to minimise any drop in conversion/yield over a series of pulses at a single temperature. These results show that deposited carbon which was in a 'hydrogenated' state increased activity as defined by turnover frequency. An increased hydrogen pressure was required at high temperatures to maintain the deposit in the 'hydrogenated' state and hence maintain catalytic activity. This behaviour agrees with the

concept proposed by Thomson and Webb[11] that the carbonaceous deposit acts as a hydrogen transfer agent. Jackson and Kelly[56] concluded that the species which may be central to the catalysis when in the 'hydrogenated' form, ceased to function as a hydrogen transfer agent and acted as a catalyst poison when dehydrogenated.

1.4 THE USE OF ISOTOPES IN THE STUDY OF HETEROGENEOUS CATALYSIS

The use of isotopes has been of major importance in mechanistic studies of heterogeneous catalysis since deuterium became available in the early 1930's.[57] In a review concerning the uses of deuterium in the study of heterogeneous catalysis, Burwell[58] found that deuterium can be used in a variety of different ways:

1. In isotopic exchange reactions.
2. To determine stereochemical aspects of exchange reactions.
3. To hydrogenate unsaturated molecules, allowing investigation of any accompanying isomerisation.
4. To determine the nature of surface hydrogen atoms.

Specifically deuterium labelled molecules, for example perdeutero propane, can be used to trace the course of a reaction and to provide information about the identity of the rate limiting step by using kinetic isotope effects. For example, Dent and Kokes[59] used $CH_2{=}CHCD_3$ and

$CD_2=CHCH_3$ to show that heterolytic dissociative adsorption of propene on zinc oxide proceeds by loss of H^+ from the methyl group.

The kinetic isotope effect[60] between hydrogen and deuterium can be used to identify a rate limiting step. In general, because of the lower zero point energy, cleavage of D-X will involve a larger activation energy and be slower than cleavage of H-X. Therefore, a large isotope effect should appear if cleavage of this bond is rate limiting. Meyer and Kemball[61] compared the rate of exchange between *n*-C_6H_{14} and D_2 with that between C_6D_{14} and H_2 on palladium. These workers found that the activation energy for reaction of C_6D_{14} was about 2 kcal greater than that for C_6H_{14} indicating that the rate limiting step is the rate of cleavage of C-H, i.e. dissociative adsorption of hexane.

Isotopes of carbon have most commonly been used as isotopic tracers - seeing which carbon atoms end up where.[62]

1.5 EARLY WORK ON TRANSHYDROGENATION

Early work investigating the transhydrogenation process was carried out by McLellan (Chemistry Department, University of Glasgow).[63] McLellan investigated the dehydrogenation of unlabelled and perdeutero propane over Pt/alumina and chromia/alumina at 400°C, 450°C, 500°C and 550°C. He also investigated the hydrogenation of propyne on chromia/alumina at 450°C.

When alternate pulses of perdeutero and unlabelled propane were passed over Pt/alumina at 400°C, 450°C, 500°C and 550°C the main reaction which took place was dissociation of propane. At 400°C some propane remained unreacted. Mass spectral data for the methane produced during these reactions showed that CH_4 was the most abundant isotopic methane regardless of whether perdeutero propane or unlabelled propane was used as the adsorbate. Small amounts of CH_3D, CH_2D_2, CHD_3 and CD_4 were also observed. Carbon and hydrogen were both lost to the catalyst during each experiment. Treating the used catalysts with dioxygen at 400°C produced small amounts of carbon dioxide.

When alternate pulses of perdeutero propane and unlabelled propane were passed over chromia/alumina at 450°C, 500°C and 550°C some dissociation of propane was observed, some propane was dehydrogenated to propene and some propane remained unreacted. Although moderate quantities of propene were monitored by combined G.C.-M.S. when unlabelled propane was used as the adsorbate, this alkene was only detected by scanning mass spectrometry when the adsorbate used was perdeutero propane. The amount of propene produced, as a percentage of the C_3-components in the product mixture is given in Table 1.1.

Table 1.1 Propene Produced, as a Percentage of C_3-Components in the Product Mixture, During Dehydrogenation of Perdeutero and Unlabelled Propane over Chromia/alumina.

PULSE	Experiment CADPR.11 450°C	Experiment CADPR.14 500°C	Experiment CADPR.13 550°C
1 (C_3D_8)	0	0	0
2 (C_3H_8)	18.8	33.2	50.3
3 (C_3D_8)	0	0	0
4 (C_3H_8)	18.1	33.8	51.3
5 (C_3D_8)	0	0	0
6 (C_3H_8)	19.2	34.7	51.2

Mass spectral data for these experiments showed that when perdeutero propane was used as the adsorbate the products were isotopic methanes (mainly CH_4), C_3D_7H and C_3D_8. When unlabelled propane was used as the adsorbate the products were isotopic methanes, $C_3H_4D_2$, C_3H_5D, C_3H_6, $C_3H_6D_2$, C_3H_7D, and C_3H_8. From these results McLellan concluded that single, perhaps even double, deuterium/hydrogen exchange was observed for both propene and propane desorbing from chromia/alumina. This exchange chiefly occurred during pulsing with unlabelled propane and was prevalent at the two highest temperatures, namely 500°C and 550°C. Carbon and hydrogen were both lost to the surface of the catalyst during each experiment. When the used catalysts were treated with dioxygen at 400°C small amounts of carbon dioxide

were produced. It was also apparent that significant amounts of dioxygen were taken up by the catalyst, probably within both the catalyst and its carbonaceous coating.

When propyne was passed over chromia/alumina at 450°C the products were carbon monoxide, methane and small amounts of propene. Significant amounts of carbon and small amounts of hydrogen were lost to the catalyst on each pulse.

Chapter TWO

OBJECTIVES

The main objective of this work was to investigate the deactivation phenomena associated with the interaction of alkanes and alkynes with platinum and chromia catalysts with a view to establishing conditions under which transhydrogenation could be effected.

For transhydrogenation to occur it must be possible to (a) dehydrogenate the alkane and (b) hydrogenate the alkyne or diene, under similar experimental conditions. Thermodynamically, dehydrogenation requires high temperatures to achieve measurable equilibrium yields of alkene. However, the use of such high temperatures results in extensive dissociation of the hydrocarbon and consequential coking of the catalyst surface. A problem which is more acute with unsaturated hydrocarbons than with alkanes.

Initially, investigations of the alkane dehydrogenation reaction were carried out using ^{13}C- and ^{2}H-stable isotope techniques to (a) establish the origins and fates of the carbon and hydrogen during the reaction and (b) obtain a detailed understanding of the mechanism including the coking process. These investigations were carried out using Pt/alumina and chromia/alumina catalysts in the temperature range 500°C to 600°C.

The next stage of the work was then to investigate the hydrogenation of propyne on these catalysts in the same temperature range. ^{2}H stable isotope techniques were used to investigate the effect

of hydrogen retained on the catalyst during the reduction process on the hydrogenation reaction.

The final stage of the work was to investigate the possibility of transhydrogenation occurring on Pt/alumina and chromia/alumina catalysts in the temperature range 500°C to 600°C. ^{2}H-stable isotope techniques were used to investigate what role hydrogen played in the reaction.

Chapter THREE

EXPERIMENTAL

3.1 INTRODUCTION

As it is impossible to look at all transhydrogenation reactions the reaction between propane and propyne has been chosen for this investigation.

$$\text{PROPANE} + \text{PROPYNE} \rightarrow 2\ \text{PROPENE}$$

As well as being representative of transhydrogenation, by virtue of its simplicity, this reaction provides various experimental advantages.

Three catalysts, platinum/alumina (Pt/alumina), chromia/alumina and chromia/alumina promoted with potassium (chromia/K/alumina), were prepared by wet impregnation by I.C.I. Katalco.

Characterisation of the catalysts, which included micromeritics, transmission electron microscopy (T.E.M.), x-ray diffraction (X.R.D.), thermal gravimetric analysis (T.G.A.) and x-ray photoelectron spectroscopy (X.P.S.), was carried out by I.C.I. Katalco. A summary of some of these results is given later in this chapter (Section 3.2.1).

The catalysts were tested for dehydrogenation, hydrogenation and transhydrogenation activity using a specially designed gas adsorption apparatus. Products of reactions were analysed by combined on-line gas chromatography/quadrupole mass spectrometry (G.C.-M.S.). The used catalysts were then treated with dioxygen in an attempt to burn off any carbon deposited on the catalyst surface during the reaction.

Dioxygen adsorption experiments were also carried out to

(a) determine the degree of reduction of each catalyst and (b) ensure that the catalysts were reduced to the same extent in each experiment.

3.2 MATERIALS

3.2.1 Catalysts

The three catalysts used in this study were prepared by wet impregnation by I.C.I. Katalco. The active phases of the three catalysts are outlined in Table 3.1. The precursors to these species were H_2PtCl_6, $(NH_4)_2Cr_2O_7$ and KOH.

Table 3.1 Active Phases of Catalysts

CATALYST	% ACTIVE PHASE	PREPARATION METHOD
Pt/alumina	0.65 Pt	Single impregnation
Chromia/alumina	9.1 Cr	Single impregnation
Chromia/K/alumina	12.7 Cr 0.8 K	Coimpregnation $(NH_4)_2Cr_2O_7$/KOH

Characterisation of the catalysts, which was carried out by I.C.I Katalco, included micromeritics, transmission electron microscopy (T.E.M.), x-ray diffraction (X.R.D.), thermal gravimetric analysis (T.G.A.) and x-ray photoelectron spectroscopy (X.P.S.).

Table 3.2 Micromeritics Results

	Total Surface Area Calculated m^2g^{-1}	Average Pore Size Å rad
Harshaw Alumina Support	217	58
Pt/alumina	203	60
Chromia/alumina	168	88
Chromia/K/alumina	not determined	not determined

Transmission electron microscopy showed:-

Pt/alumina - the support appears to show very porous particles assumed to be gamma alumina. The catalyst contains some rounded electron dense particles up to 200 Å which are presumed to contain platinum. These large particles do not appear to be present in the reduced catalyst.

Chromia/alumina - the support shows very porous gamma alumina particles. There was no visible evidence of chromium in the unused catalyst. However, in a catalyst sample which had been used for dehydrogenation, there appears to be a denser area in the gamma alumina aggregates which could be chromium or chromium oxide.

X-ray diffraction analysis of the chromia/alumina catalyst confirmed that the support was gamma alumina and that poorly crystalline Cr_2O_3 was the only detectable chromia phase.

Thermogravimetric analysis of the chromia/alumina and chromia/K/alumina catalysts was performed in dinitrogen and in dihydrogen/dinitrogen. The chromia/alumina catalyst in dinitrogen exhibited a steady weight loss. A similar underlying loss was observed when the carrier gas was dihydrogen/dinitrogen but a possible reduction step was detected at 325°C. Similar behaviour was observed with the chromia/K/alumina catalyst.

A summary of the x-ray photoelectron spectroscopy results is given in Table 3.3.

Table 3.3 X-Ray Photoelectron Spectroscopy Quantitation Results.

Atomic %

	Cr 2p	O 1s	K 2p	Pt 4d	C 1s	Al 2p
Harshaw Alumina Support		61.0			3.3	35.7
Pt/alumina		59.7		0.5	3.1	36.6
Chromia/K/alumina	5.3	57.5	1.1		3.2	32.9

3.2.2 Gases

There were four hydrocarbons used in the adsorption experiments. They were unlabelled propane (British Oxygen Company, hereafter referred to as B.O.C., minimum 99% pure), propane-d_8 (Cambridge

Isotope Laboratories, 98% pure), (2-^{13}C)-propane (C/D/N Isotopes Inc., 99.1 atom % ^{13}C) and unlabelled propyne (B.D.H. Chemicals Ltd., minimum assay 96%pure).

The dioxygen used in the adsorption experiments was supplied by B.O.C. (minimum 99.5% pure).

3.3 GAS ADSORPTION APPARATUS

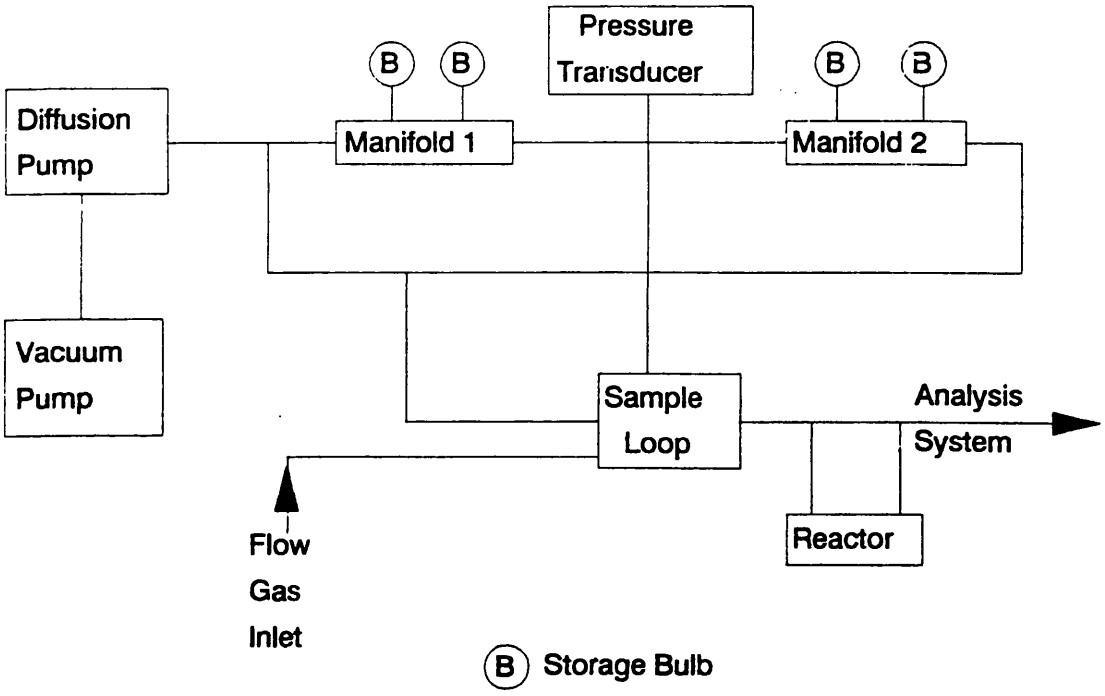
All adsorption experiments were carried out using the gas adsorption apparatus. This gas adsorption apparatus consisted of two main sections: the vacuum-flow system and the analysis system.

3.3.1 The Vacuum-Flow System

The vacuum-flow system, shown schematically in Figure 3.1, consisted of two distinct sections - (a) the vacuum section and (b) the flow section. The only overlap between the two sections was the sample loop.

In the vacuum section, the vacuum was maintained at pressures less than 10^{-4} torr by means of a mercury diffusion pump backed by a rotary oil pump. The vacuum was continually monitored using a pressure transducer (Edwards medium vacuum control unit 251, Edwards High Vacuum International).

Figure 3.1 Schematic Diagram of the Vacuum-Flow Section

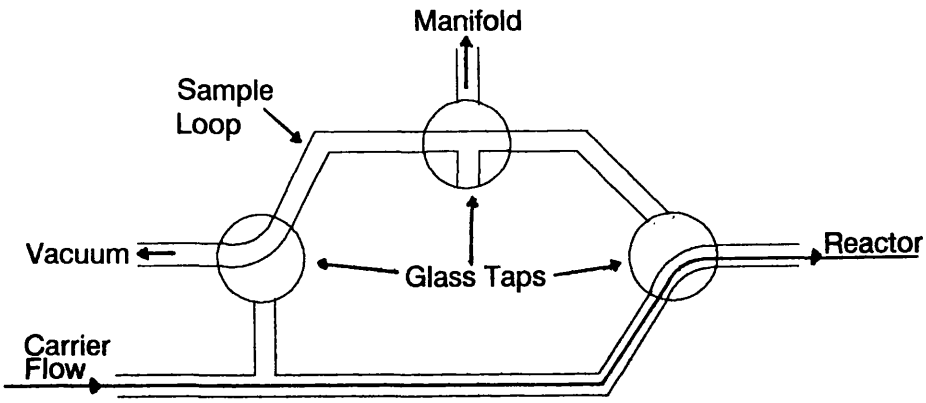


Gases were stored in four one litre storage bulbs, each of which was connected to one of the two manifolds to allow ease of filling and evacuation. There were also two socket connections to allow attachment of storage bulbs containing labelled gases.

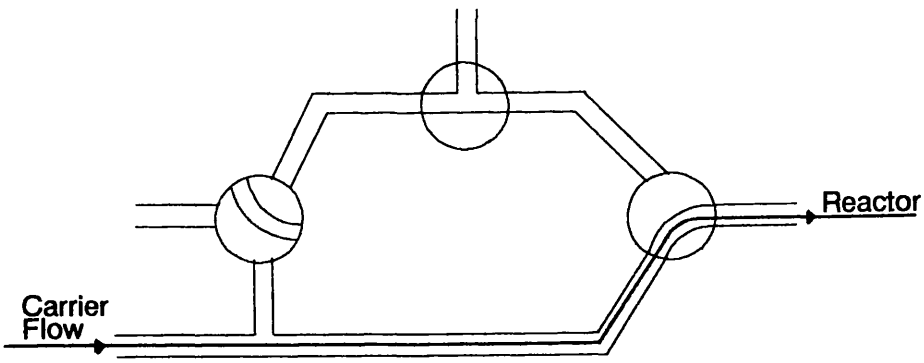
The sample loop consisted of three spring loaded glass taps. Gases were admitted into the evacuated sample loop (Figure 3.2a), of which the exact volume was known, by closing the taps to the vacuum pump system (Figure 3.2b) and allowing the required pressure of gas into the system by opening the relevant storage bulb. The pressure of gas admitted was monitored using the pressure transducer. From the sample loop the gas was injected into the helium carrier gas flow (Figure 3.2c).

Figure 3.2 The Sample Loop.

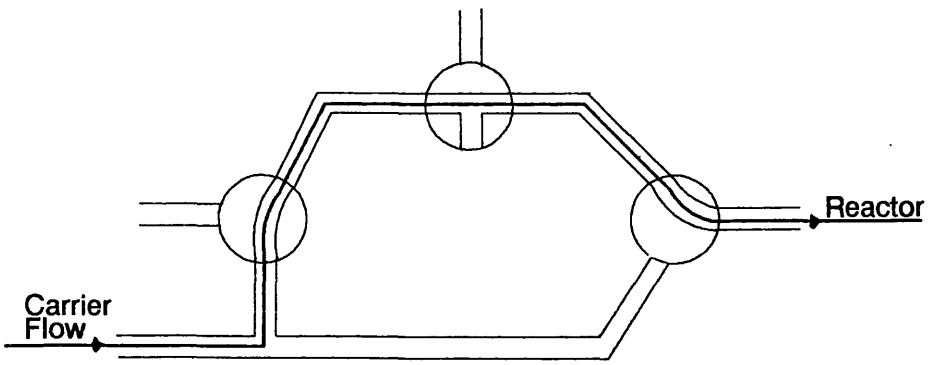
(a) Evacuating Sample Loop.



(b) Loading Sample.



(c) Injecting Sample.



The reactor section is shown in Figure 3.3. The catalyst sample (typically 0.2 g) was supported on a silica sinter. The reactor temperature was measured with a Cr/Al thermocouple inserted level with the catalyst sample and attached to a Comark electronic thermometer. The reactor section was heated by a Watlow furnace controlled by a Eurotherm 818 Temperature Programmer. After being passed through the reactor the resultant products were then carried, in the helium stream, to the analysis system.

3.3.2 The Analysis System

The analysis system consisted of a gas chromatograph and a quadrupole mass spectrometer. Figure 3.4 shows the arrangement of the analysis system in relation to the gas adsorption apparatus.

The gas chromatographic system consisted of a Shimadzu GC-14A chromatograph fitted with a thermal conductivity detector (T.C.D.), a Chromjet integrator and a computer system with LABNET attached. The G.C. column itself was a 2.2 m stainless steel column, diameter 1/8th inch, packed with Poropak QS 50 - 80 mesh, which allowed separation of simple hydrocarbons. The products were eluted from the column in the order

dioxygen < carbon monoxide < methane < carbon dioxide < ethane < propene < propane < propyne.

Figure 3.3 The Reactor System.

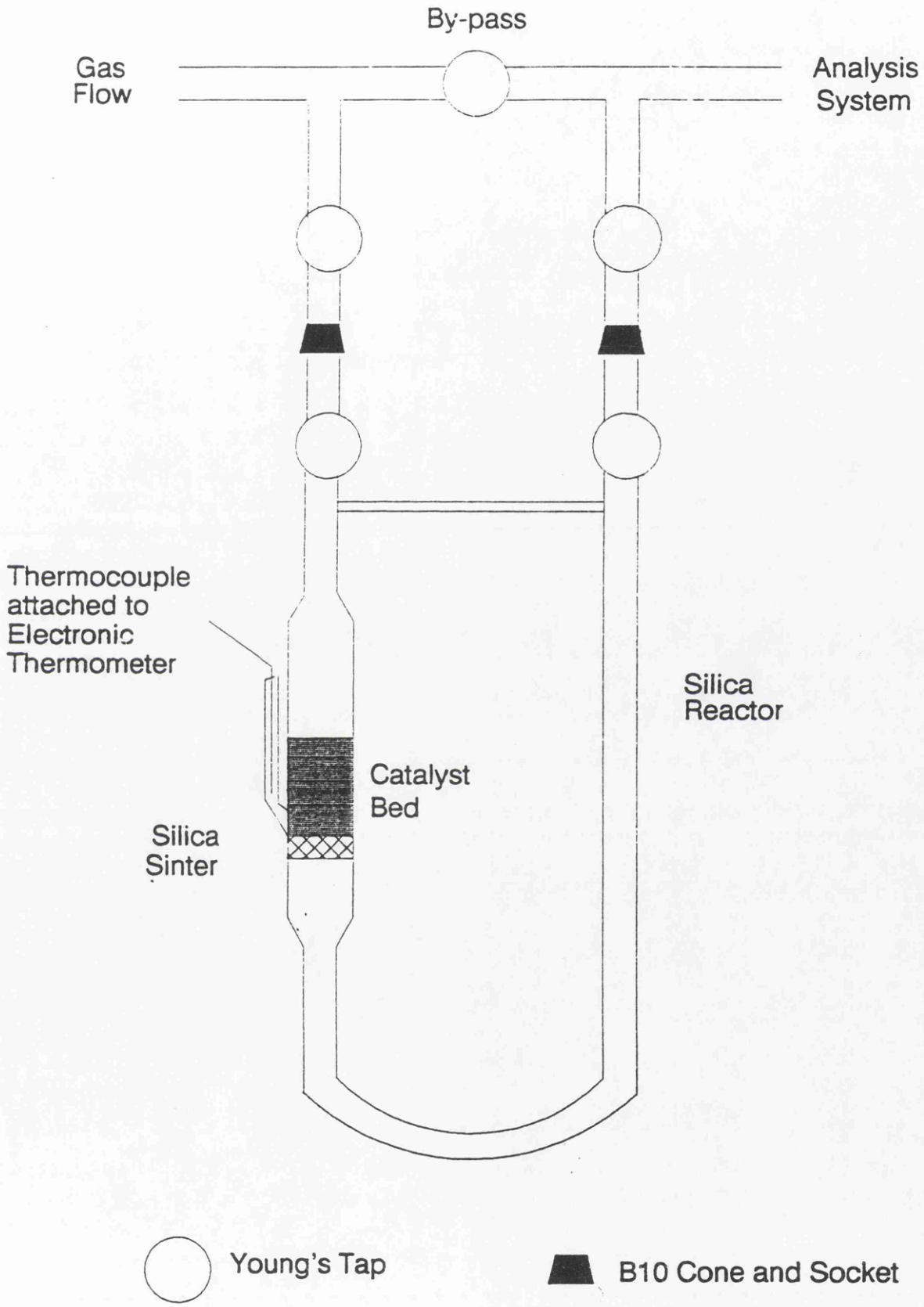
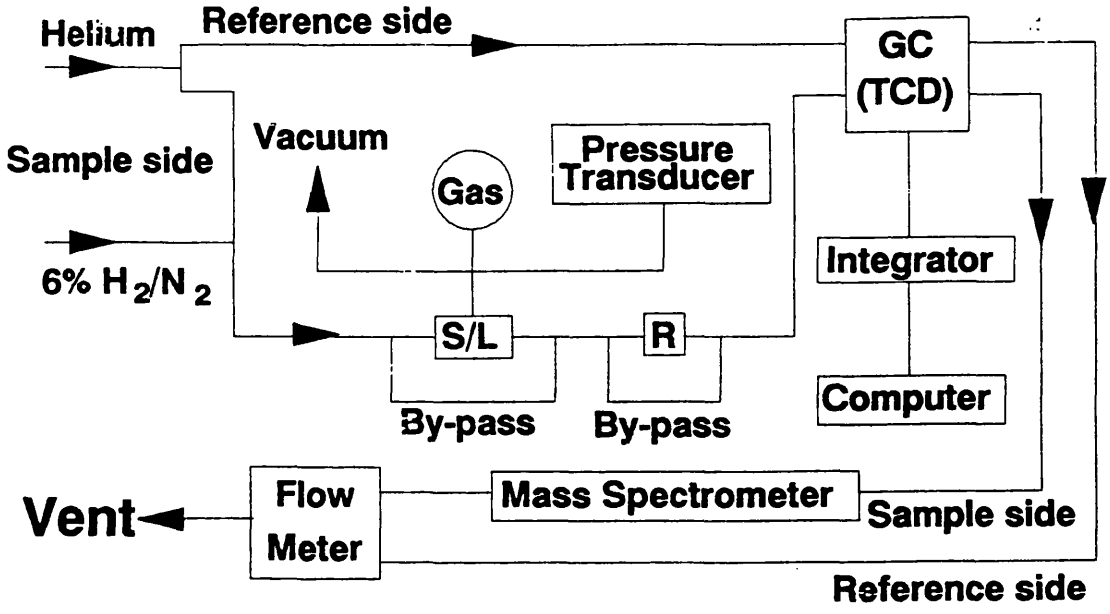


Figure 3.4 Schematic Diagram of Gas Adsorption Apparatus.



S/L = sample loop R = reactor

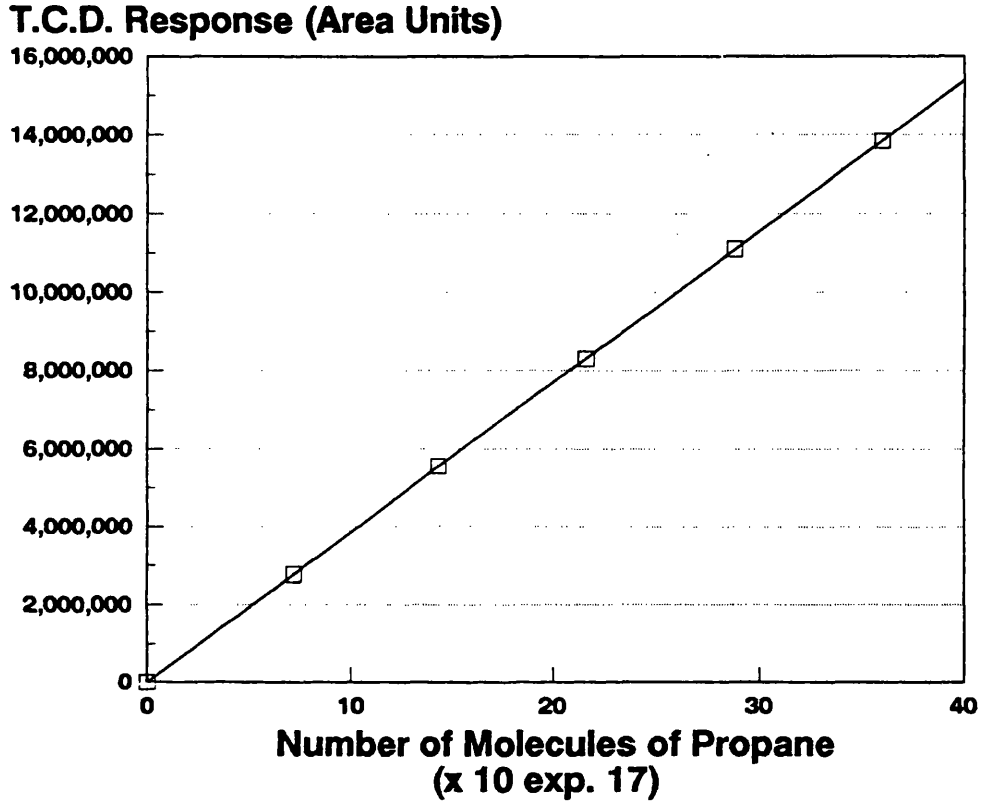
When a perdeutero hydrocarbon was used it had a shorter retention time than the corresponding unlabelled hydrocarbon.

As each product was eluted from the column, the signal change detected on the T.C.D. was amplified. The amplified signal was then detected by the chart recorder which plotted the change in signal for each product, as a peak, with time. The integrator calculated the area of the peak and this value was tabulated against its corresponding retention time.

To calibrate the system, known pressures of each product gas were admitted into the sample loop, injected into the carrier gas stream and passed through the column. A range of pressures was used to verify

the linear response of the detector. A typical calibration graph is shown in Figure 3.5.

Figure 3.5 Calibration Graph for Propane.



From these results a response factor was calculated for each gas (Table 3.4) relating its peak area to a number of moles such that,

no. of moles of gas = response factor x area.

Having been vented from the G.C. the carrier gas flow, containing the separated products, was split and a small amount was bled, through a Hoke needle valve, into the mass spectrometer.

Table 3.4 Gas Chromatograph Response Factors.

Gas	Retention Time (minutes)	Response Factor (no.of moles/area units x 10^{11})
Carbon monoxide	1.10	4.26
Methane	1.41	4.80
Carbon Dioxide	1.93	3.63
Ethane	4.06	3.19
Propyne	22.25	2.80
Propene	16.20	2.66
Propane	19.29	2.60
D_6-Propene	14.82	2.74
D_8-Propane	17.59	2.70
Dioxygen	0.85	4.74

As with all mass spectrometers, the Spectramass Selector used consisted of 3 main components:-

(1) The ION SOURCE which produced ions that were representative of the gases in the environment, then focused and injected these ions into the mass analyser.

(2) The MASS ANALYSER which separated ions of different mass/charge ratio and presented the selected ions to the detector.

(3) The DETECTOR which collected the separated ions. Provision was made to eliminate stray particles.

The output was in the form of peaks on a Goerz Metrawatt SE430

chart recorder. In this case the peak height represents the partial pressure of a particular mass/charge (m/z) ratio. Peak heights were measured manually and tabulated. Scanning across each G.C. peak allowed for possible isotopic separation.

The mass spectrometer was calibrated by injecting several samples of each reactant gas into the helium carrier gas and measuring the resultant fragmentation pattern. The fragmentation patterns for propane, perdeutero propane, (2-^{13}C)-propane and propyne are given in Table 3.5.

3.4 REACTION PROCEDURE

3.4.1 Gas Supply

Before use the reduction gas, 6% H_2/N_2 (B.O.C.), or D_2 (B.D.H. Chemicals Ltd., 99.5% pure) and the carrier gas, He (B.O.C., 99.995% pure), were purified by passage through a deoxygenating catalyst and then molecular sieves. The deoxygenating catalyst was prepared by dissolving a known weight of palladium (II) chloride (0.34 g) in water and impregnating the resultant solution on to tungsten (VI) oxide (20 g), the water was then removed using a rotary evaporator. The catalyst was then placed in a small glass vessel and activated by passing hydrogen gas over it for 60 minutes. After passage through the deoxygenator the gases were dried using Linde 5A molecular sieves contained in a brass cylinder. The molecular sieves were regenerated by heating to 150°C

Table 3.5 Fragmentation Patterns for Propane, Perdeutero Propane (2-^{13}C)-Propane and Propyne.

m/z	Propane	D_8-Propane	(2-^{13}C)-Propane	Propyne
36	0.10	0.00	0.00	0.05
37	0.19	0.00	0.02	0.20
38	0.29	0.00	0.15	0.28
39	0.76	0.00	0.20	0.79
40	0.24	0.00	0.74	1.00
41	0.67	0.00	0.07	0.35
42	0.24	0.60	0.54	0.02
43	0.95	0.00	0.15	0.00
44	1.00	0.00	0.83	0.00
45	0.05	0.00	1.00	0.00
46	0.00	0.50	0.00	0.00
47	0.00	0.00	0.00	0.00
48	0.00	0.10	0.00	0.00
49	0.00	0.00	0.00	0.00
50	0.00	0.70	0.00	0.00
51	0.00	0.00	0.00	0.00
52	0.00	1.00	0.00	0.00

every two weeks.

The gas flow was monitored using a bubble flow meter attached to the effluent stream. The gas flow could be adjusted using a needle valve.

3.4.2 Standard Reduction

A standard reduction procedure was used to activate the catalyst samples for both the dioxygen and the hydrocarbon adsorption experiments. This was as follows:-

(1) the catalyst sample was heated to 600°C at a heating rate of 20° min^{-1} in a flow of reduction gas of 25 ml min^{-1}.

(2) the catalyst sample was then held at this temperature in flowing reduction gas for 15 minutes.

3.4.3 Adsorption of Dioxygen

After a standard reduction (Section 3.4.2) the gas stream was changed to helium at a flow rate of 25 ml min^{-1}. The catalyst samples were held at 600°C. Fixed pulses of dioxygen were then injected over the reduced catalyst sample in the flow of helium. The T.C.D. detected the dioxygen that was not adsorbed by the catalyst sample. Initially the dioxygen was almost entirely adsorbed by the catalyst and, therefore, produced the smallest peaks. Subsequent pulses produced increasingly

large peaks. Pulsing was continued until three sequential peaks of approximately the same area were obtained, indicating that the catalyst had been completely reoxidised.

3.4.4 Adsorption of Hydrocarbons

After a standard reduction in either 6% H_2/N_2 (25 ml min^{-1}) or D_2 (25 ml min^{-1}) the gas stream was changed to helium and the catalyst charge was purged while its temperature was adjusted (normally lowered) to the appropriate adsorption temperature. The catalyst was then held at this temperature, under the helium flow, for an hour before the first pulse of hydrocarbon was passed over it.

Three sets of adsorption experiments were carried out (a) dehydrogenation, (b) hydrogenation and (c) transhydrogenation.

(a) Dehydrogenation

Experiments PADPR.01 - PADPR.03 and CADPR.11 - C(K)ADPR.13

Propane-d_8 and unlabelled propane were alternately passed over the reduced catalyst charge at one of three temperatures, 500°C, 550°C or 600°C, as pulses of 25 mbar pressure in 5.83 cm^3.

Experiments PACPR.01 and C(K)ACPR.01 - C(K)ACPR.02

Unlabelled propane and (2-^{13}C)-propane were passed over the

reduced catalyst charge at one of three temperatures, 500°C, 550°C or 600°C, as pulses of 25 mbar pressure in 5.83 cm^3.

(b) Hydrogenation

Experiments PAPRY.01 - C(K)APRY.03

Six pulses of propyne were passed over the reduced catalyst charge at one of three temperatures, 500°C, 550°C or 600°C, as pulses of 25 mbar pressure in 5.83 cm^3.

Experiment C(K)ADPRY.01

Three pulses of propyne were passed over a deuterium reduced catalyst charge at 600°C as pulses of 25 mbar pressure in 5.83 cm^3.

(c) Transhydrogenation

Experiments PADTH.01 - C(K)ADTH.07

Six pulses of 1:1 propane-d_8:propyne were passed over the reduced catalyst charge at one of four temperatures, 400°C, 500°C, 550°C or 600°C, as pulses of 25 mbar pressure in 5.83 cm^3.

Experiment C(K)ATH.01

Six pulses of 1:1 propane:propyne were passed over a reduced catalyst charge at 550°C as pulses of 25 mbar pressure in 5.83 cm^3.

Experiment C(K)ATH.02

Six pulses of 1:1 propane:propyne were passed over a reduced catalyst charge at 550°C as pulses of 50 mbar pressure in 5.83 cm^3.

3.4.5 Treatment of Used Catalysts With Dioxygen

Typically 30 minutes after the last hydrocarbon pulse, several pulses of dioxygen of 25 mbar pressure in 5.83 cm^3 were passed in succession over the used catalyst at the adsorption temperature.

Chapter FOUR

TREATMENT OF RESULTS

4.1 DIOXYGEN ADSORPTION

Dioxygen adsorption experiments were carried out in the vacuum flow system described in Section 3.3 following the procedure described in Section 3.4.3. A known pressure of dioxygen was pulsed over the reduced catalyst sample in a flow of helium. A T.C.D. was used to detect any dioxygen that was not adsorbed by the catalyst sample.

From the size of the sample loop (V = 5.83 ml) and the pressure of dioxygen used (P = 25 mbar), the number of moles of dioxygen injected into the helium carrier stream per pulse could be calculated from the gas equation

$$n = \frac{PV}{RT} \qquad (1)$$

where n = number of moles of dioxygen

R = gas constant

T = absolute temperature.

By multiplying the number of moles of dioxygen by Avogadro's number, the number of molecules of dioxygen injected per pulse was calculated.

Dioxygen was pulsed over the catalyst until three sequential peaks of approximately the same area were obtained by the T.C.D., indicating that the catalyst was completely reoxidised. From the T.C.D. peak areas of the dioxygen pulses prior to complete reoxidation the total

number of dioxygen molecules adsorbed by the catalyst was calculated from the equation

$$molecules\ of\ O_2\ adsorbed\ by\ catalyst = \sum_{i=1}^{i=n} molecules\ of\ O_2\ per\ pulse\ x\ (1 - \frac{peak\ area\ i}{peak\ area\ n})$$

where n = number of pulses required to reach complete reoxidation

The ratio of the number of metal atoms in the catalyst sample to the number of atoms of oxygen adsorbed was then calculated.

4.2 ADSORPTION OF HYDROCARBONS

Hydrocarbon adsorption experiments were carried out using the vacuum-flow system described in Section 3.3 following the procedure described in Section 3.4.4. A known pressure of hydrocarbon was pulsed over the reduced catalyst sample in a flow of helium. The products were then analysed by combined on-line gas chromatography-quadrupole mass spectrometry (Section 3.3.2).

4.2.1 Product Distribution

The results from the G.C. analyses were used to calculate product distributions. A standard procedure was adopted to minimise inconsistencies.

Before each experiment two bypass pulses of each adsorption gas

were measured. From the size of the sample loop (V = 5.83 ml) and the pressure of gas used, the number of moles of gas injected into the helium carrier gas stream per pulse could be calculated from the gas equation (1).

By multiplying the number of moles of gas by Avogadro's number, the number of molecules of gas injected per pulse was calculated. The average of the two T.C.D. peak areas was calculated. The average number of molecules of a particular adsorption gas per unit area ($\overline{N}_{ADS.\ GAS}$) was then calculated by dividing the number of molecules of adsorption gas by the T.C.D. peak area.

For each pulse during the adsorption experiment the T.C.D. peak area of each product was tabulated against its corresponding retention time. The following equation was used to convert the T.C.D. peak area into number of molecules of product

$$N_{PRODUCT} = Area_{PRODUCT} \times RF_{PRODUCT} \times \frac{\overline{N}_{ADS.\ GAS}}{RF_{ADS.GAS}}$$

where $N_{PRODUCT}$ = number of molecules of product

$Area_{PRODUCT}$ = T.C.D. area of product

$RF_{PRODUCT}$ = response factor of product (Table 3.4)

$\overline{N}_{ADS.\ GAS}$ = average number of molecules of adsorption gas per unit area

$RF_{ADS.\ GAS}$ = response factor of adsorption gas (Table 3.4)

So, for example, for carbon monoxide produced from unlabelled propane the relevant equation would be

$$N_{CO} = Area_{CO} \times 4.26 \times \frac{\bar{N}_{C_3H_8}}{2.60}$$

This procedure was repeated for each product on each pulse to give the product distribution for the experiment.

4.2.2 Carbon Balance

As the number of molecules of gas per pulse was known, the number of carbon atoms per pulse could be calculated simply by multiplying the number of molecules by 3. This value is tabulated as 'Carbon In'. The value of 'Carbon Out' was calculated using the product distribution. The number of molecules of a particular product was multiplied by the number of carbon atoms per molecule and the sum of all carbon atoms in all the products on a particular pulse was calculated. 'Delta Carbon' is the difference between 'Carbon In' and 'Carbon Out'. Therefore, a negative value for delta carbon means that carbon was lost to the catalyst and a positive value for delta carbon means that carbon was gained from the catalyst.

4.2.3 Hydrogen Balance

The hydrogen balance for each experiment was calculated using the same method as for the carbon balance.

4.2.4 Mass Spectra

The output from the mass spectrometer was in the form of peaks on a chart recorder. The peak height represents the partial pressure of a particular mass/charge (m/z) ratio. Peak heights were measured manually and tabulated against mass/charge ratio. Scanning across the G.C. peak allowed for possible isotopic separation.

Before each scan a background reading was taken. G.C. peaks were scanned across the relevant m/z range over an appropriate time interval. Peak heights were measured for each interval. An average value for the peak height of each m/z was then taken from all the intervals across the G.C. peak. The background reading was then subtracted to give a background corrected value for each m/z value in the relevant range.

(a) Experiments Using Deuterium

When either deuterated propane was used in an experiment or when the catalyst was reduced in deuterium the following method was used to analyse mass spectra.

Isotopic Methanes

The methane peak was scanned across the range m/z 15 - 20 at 10 second intervals. The ratio of isotopic methanes produced was calculated using the data in Table 4.1.[64]

Table 4.1 Mass Spectra of Isotopic Methanes

m/z	CD_4	CD_3H	CD_2H_2	CDH_3	CH_4
20	100	0	0	0	0
19	0	100	0	0	0
18	53	28	100	0	0
17	0	51	62	100	0
16	12	13	31	77	100

Assuming that the background corrected peak height of m/z 20 was entirely due to the presence of CD_4 the data in the above table was then used to calculate the fragmentation pattern due to CD_4. This fragmentation pattern was then subtracted from each of the other m/z values in the range. The peak height of m/z 19 was assumed to be due to the presence of CD_3H and the above data was used to calculate its fragmentation pattern. This fragmentation pattern was then subtracted from the other m/z values in the range. This procedure was repeated for each isotopic methane to give a value for the peak height of the parent

ion for each methane. These values were then summed and converted to percentages which in turn were used to give the calculated ratio of isotopic methanes.

Propene

The propene peak was scanned across the range m/z 36 - 52 at 30 second intervals.

Background corrected peak heights were normalised to m/z 41 for pulses of unlabelled propane and m/z 46 for pulses of deuterated propane.

For transhydrogenation experiments background corrected peak heights were normalised to m/z 41.

For comparison purposes the fragmentation patterns for unlabelled propene and perdeutero propene are given in Table 4.2.

Table 4.2 Mass Spectra For Unlabelled and Perdeutero Propene

m/z	Unlabelled Propene C_3H_6	Deuterated Propene C_3D_6
36	0.00	0.00
37	0.19	0.30
38	0.22	0.20
39	0.97	0.10
40	0.38	0.10
41	1.00	0.10
42	0.65	0.60
43	0.00	0.20
44	0.22	0.30
45	0.00	0.10
46	0.00	1.00
47	0.00	0.00
48	0.00	0.60
49	0.00	0.00
50	0.00	0.00

Propane

The propane peak was also scanned across the range m/z 36 - 52 at 30 second intervals.

For dehydrogenation experiments the fragmentation pattern of the relevant adsorption gas was subtracted. Corrected peak heights were then normalised to m/z 43 for pulses of unlabelled propane and m/z 51 for pulses of deuterated propane.

For transhydrogenation experiments the fragmentation pattern of deuterated propane was subtracted and the corrected peak heights were normalised to m/z 51.

Experiments Using ^{13}Carbon

When (2-^{13}C)-propane was used in an experiment the following method was used to analyse the mass spectra.

Methane

The methane peak was scanned across the range m/z 15 - 20 at 10 second intervals. Any contribution made to the background corrected peak height of m/z 16 from the fragmentation of ^{13}C-methane was subtracted. This corrected value along with the height of m/z 17 were used to calculate the ratio of $^{12}CH_4$ to $^{13}CH_4$.

Carbon Monoxide and Carbon Dioxide

Both the carbon monoxide and carbon dioxide peaks were scanned across the range m/z 16 - 46 at 30 second intervals. The background corrected peak heights of m/z 28 and m/z 29 were used to calculate the ratio of ^{12}CO:^{13}CO. Similarly, the background corrected peak heights of m/z 44 and m/z 45 were used to calculate the ratio of $^{12}CO_2$:$^{13}CO_2$.

Propene and Propane

The propene and propane peaks were scanned across the range m/z 36 - 46 at 10 second intervals. Background corrected peaks were normalised to the principal ion in the range.

4.3 TREATMENT OF USED CATALYSTS WITH DIOXYGEN

After each experiment the used catalyst was treated with dioxygen to see how much, if any, carbon could be burnt off the catalyst as carbon monoxide or carbon dioxide.

A known pressure of dioxygen was pulsed over the used catalyst sample in a flow of helium. A T.C.D. was used to detect any carbon monoxide or carbon dioxide produced and any dioxygen that was not adsorbed by the catalyst.

Using the procedure outlined in Section 4.2.1 the product distribution for the interaction of oxygen with the used catalyst was calculated. Once the amount of carbon monoxide, oxygen and carbon dioxide had been quantified a simple subtraction allowed the calculation of the amount of oxygen taken up by the catalyst.

Chapter FIVE

RESULTS

5.1 DIOXYGEN ADSORPTION

Dioxygen adsorption experiments were carried out to (a) ensure the reproducibility of catalyst reduction and (b) determine the degree of reduction of each of the three catalysts. The procedure for these experiments is given in Section 3.4.3. The results of these experiments are given in Tables 5.1a - 5.3b.

Table 5.1a Oxygen Adsorption on Pt/alumina.
0.2135 g Pt/alumina which contains 4.29×10^{18} atoms Pt.

Pulse	Oxygen Taken Up By Catalyst (atoms x 10^{17})	Cummulative Oxygen Taken Up By Catalyst (atoms x 10^{17})
1 (25 mbar O_2)	28.4	28.4
2 (25 mbar O_2)	9.6	38.0
3 (25 mbar O_2)	1.0	39.0
4 (25 mbar O_2)	0.0	39.0
5 (25 mbar O_2)	0.0	39.0
6 (25 mbar O_2)	0.0	39.0

Ratio of $Pt:O_{ads}$ $= 4.29 \times 10^{18}:39.0 \times 10^{17}$
$= 1.00:0.91$

Table 5.1b Oxygen Adsorption on Pt/alumina.
0.2113 g Pt/alumina which contains 4.25×10^{18} atoms Pt.

Pulse	Oxygen Taken Up By Catalyst (atoms x 10^{17})	Cummulative Oxygen Taken Up By Catalyst (atoms x 10^{17})
1 (25 mbar O_2)	27.8	27.8
2 (25 mbar O_2)	8.6	36.4
3 (25 mbar O_2)	3.4	39.8
4 (25 mbar O_2)	3.8	43.6
5 (25 mbar O_2)	0.0	43.6
6 (25 mbar O_2)	0.0	43.6

Ratio of $Pt:O_{ads}$ $= 4.25 \times 10^{18}:43.6 \times 10^{17}$
$= 1.00:1.02$

Table 5.2 Oxygen Adsorption on Chromia/alumina.
0.2054 g Chromia/alumina which contains 2.16×10^{20} atoms Cr.

Pulse	Oxygen Taken Up By Catalyst (atoms x 10^{17})	Cummulative Oxygen Taken Up By Catalyst (atoms x 10^{17})
1 (25 mbar O_2)	35.4	35.4
2 (25 mbar O_2)	32.4	67.8
3 (25 mbar O_2)	31.0	98.8
4 (25 mbar O_2)	28.2	127.0
5 (25 mbar O_2)	27.6	154.6
6 (25 mbar O_2)	25.4	180.0
7 (25 mbar O_2)	19.8	199.8
8 (25 mbar O_2)	21.2	221.0
9 (25 mbar O_2)	28.6	249.6
10 (25 mbar O_2)	25.0	274.6
11 (25 mbar O_2)	25.6	300.2
12 (25 mbar O_2)	24.0	324.2
13 (25 mbar O_2)	19.8	344.0
14 (25 mbar O_2)	23.6	367.6
15 (25 mbar O_2)	24.4	392.0
16 (25 mbar O_2)	25.4	417.4
17 (25 mbar O_2)	24.4	441.8
18 (25 mbar O_2)	22.8	464.6
19 (25 mbar O_2)	23.2	487.8
20 (25 mbar O_2)	21.6	509.4

Ratio of $Cr:O_{ads}$ $= 2.16 \times 10^{20}:509.4 \times 10^{17}$
$= 1.00:0.24$

Table 5.3a Oxygen Adsorption on Chromia/K/alumina.
0.2129 g Chromia/K/alumina which contains 3.13×10^{20} atoms Cr.

Pulse	Oxygen Taken Up By Catalyst (atoms x 10^{17})	Cummulative Oxygen Taken Up By Catalyst (atoms x 10^{17})
1 (25 mbar O_2)	64.0	64.0
2 (25 mbar O_2)	68.2	132.2
3 (25 mbar O_2)	59.2	191.4
4 (25 mbar O_2)	60.4	251.8
5 (25 mbar O_2)	58.2	310.0
6 (25 mbar O_2)	61.6	371.6
7 (25 mbar O_2)	56.8	428.4
8 (25 mbar O_2)	46.8	475.2
9 (25 mbar O_2)	39.6	514.8
10 (25 mbar O_2)	36.0	550.8
11 (25 mbar O_2)	35.8	586.6
12 (25 mbar O_2)	29.0	615.6

Ratio of $Cr:O_{ads}$ $= 3.13 \times 10^{20}:615.6 \times 10^{17}$
$= 1.00:0.20$

Table 5.3b Oxygen Adsorption on Chromia/K/alumina.
0.2255 g Chromia/K/alumina which contains 3.31×10^{20} atoms Cr.

Pulse	Oxygen Taken Up By Catalyst (atoms x 10^{17})	Cummulative Oxygen Taken Up By Catalyst (atoms x 10^{17})
1 (25 mbar O_2)	65.2	65.2
2 (25 mbar O_2)	68.0	133.2
3 (25 mbar O_2)	68.0	201.2
4 (25 mbar O_2)	68.0	269.2
5 (25 mbar O_2)	67.8	337.0
6 (25 mbar O_2)	68.8	405.8
7 (25 mbar O_2)	69.4	475.2
8 (25 mbar O_2)	68.6	543.8
9 (25 mbar O_2)	67.8	611.6
10 (25 mbar O_2)	63.6	675.2
11 (25 mbar O_2)	54.6	729.8
12 (25 mbar O_2)	45.0	774.8

Ratio of $Cr:O_{ads}$ $= 3.31 \times 10^{20}:774.8 \times 10^{17}$
$= 1.00:0.24$

5.2 DEHYDROGENATION

Two different types of experiment were carried out to determine how active the catalysts were towards dehydrogenation. The first involved passing alternate pulses of perdeutero propane and unlabelled propane over each of the catalysts at various temperatures. The purpose of this type of experiment was to follow the hydrogen during the dehydrogenation reaction. The second type of experimment involved passing (2-^{13}C) -propane and unlabelled propane over each of the catalysts at various temperatures. The purpose of this type of experiment was to follow the carbon during the dehydrogenation reaction.

These experiments were done by passing pulses of labelled and unlabelled propane over a reduced catalyst charge at the appropriate adsorption temperature using the gas adsorption apparatus, described in Section 3.3, following the reaction procedure outlined in Section 3.4. The results of these experiments are given in Tables 5.4a - 5.13i and Figures 5.1a - 5.10c.

Note

Experimental codes used in this section are as follows:-

1. The first two, or three, letters of the code refers to the catalyst used:-

   PA = platinum/alumina

   CA = chromia/alumina

   C(K)A = chromia/alumina promoted with potassium.

2. The remaining group of letters refers to the isotopically labelled gas used in the experiment:

   DPR = perdeutero propane

   CPR = (2-^{13}C)-propane

3. Finally, the two digits at the end of the code are the experiment number for a particular catalyst and experiment type as described by the letters of the code.

Dehydrogenation Experiments

Experiment	Catalyst	Temperature	Gases
PADPR.01	Pt/alumina	500°C	C_3D_8/C_3H_8
PADPR.02	Pt/alumina	550°C	C_3D_8/C_3H_8
PADPR.03	Pt/alumina	600°C	C_3D_8/C_3H_8
PACPR.11	Pt/alumina	600°C	$C_3H_8/(2\text{-}^{13}C)\text{-}C_3H_8$
CADPR.11	Chromia/alumina	500°C	C_3D_8/C_3H_8
C(K)ADPR.11	Chromia/K/alumina	500°C	C_3D_8/C_3H_8
C(K)ADPR.12	Chromia/K/alumina	550°C	C_3D_8/C_3H_8
C(K)ADPR.13	Chromia/K/alumina	600°C	C_3D_8/C_3H_8
C(K)ACPR.01	Chromia/K/alumina	500°C	$C_3H_8/(2\text{-}^{13}C)\text{-}C_3H_8$
C(K)ACPR.02	Chromia/K/alumina	550°C	$C_3H_8/(2\text{-}^{13}C)\text{-}C_3H_8$

Experiment PADPR.01

Table 5.4a Product Distribution for the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Pt/alumina Catalyst at 500°C. (Catalyst weight = 0.2016 g; pulse size = 36.0 x 10^{17} molecules).

Product molecules x 10^{17}

Pulse	CO	CX_4	C_2X_6	C_3X_8
1(C_3D_8)	34.7	46.0	0.0	0.0
2(C_3H_8)	30.0	44.8	0.0	0.0
3(C_3D_8)	28.5	49.9	0.0	1.0
4(C_3H_8)	24.9	44.3	0.0	0.8
5(C_3D_8)	26.3	45.0	0.1	1.5
6(C_3H_8)	26.0	44.7	0.2	1.7

Table 5.4b Carbon Balance for the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Pt/alumina Catalyst at 500°C. (Catalyst weight = 0.2016 g).

Carbon atoms x 10^{17}

Pulse	Carbon In	Carbon Out	Delta Carbon
1(C_3D_8)	108.0	80.7	-27.3
2(C_3H_8)	108.0	74.8	-33.2
3(C_3D_8)	108.0	81.4	-26.6
4(C_3H_8)	108.0	71.6	-36.4
5(C_3D_8)	108.0	76.0	-32.0
6(C_3H_8)	108.0	76.2	-31.8

Total carbon lost to the catalyst = 187.3 x 10^{17} atoms.

Experiment PADPR.01

Figure 5.1a Product Distribution for the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Pt/alumina Catalyst at 500°C. (Catalyst weight = 0.2016 g; pulse size = 36.0 x 10^{17} molecules).

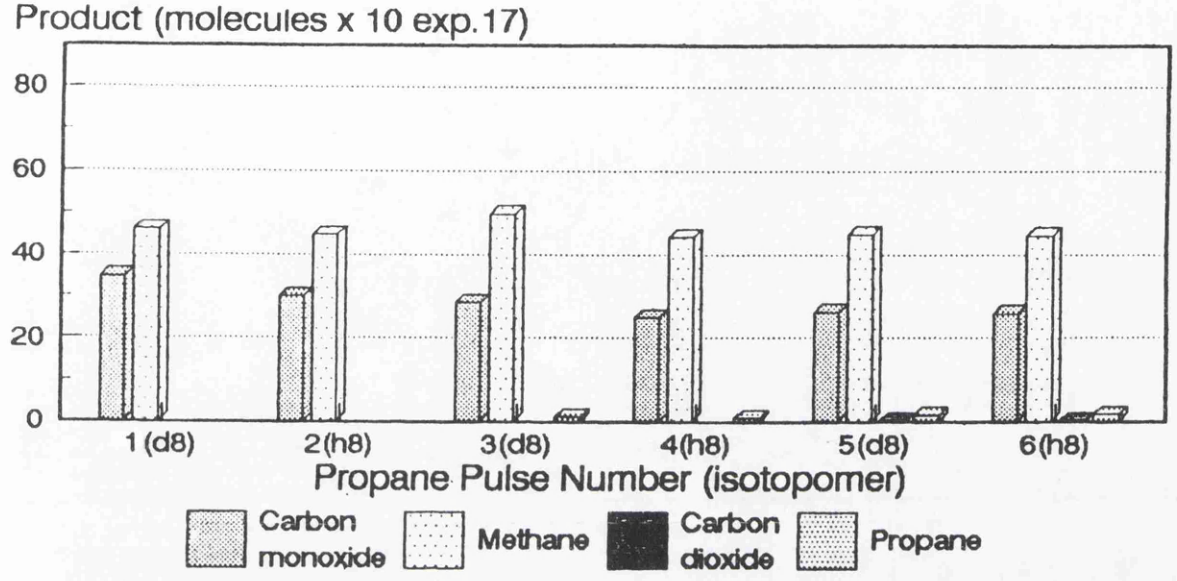


Figure 5.1b Carbon Balance for the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Pt/alumina Catalyst at 500°C. (Catalyst weight = 0.2016 g).

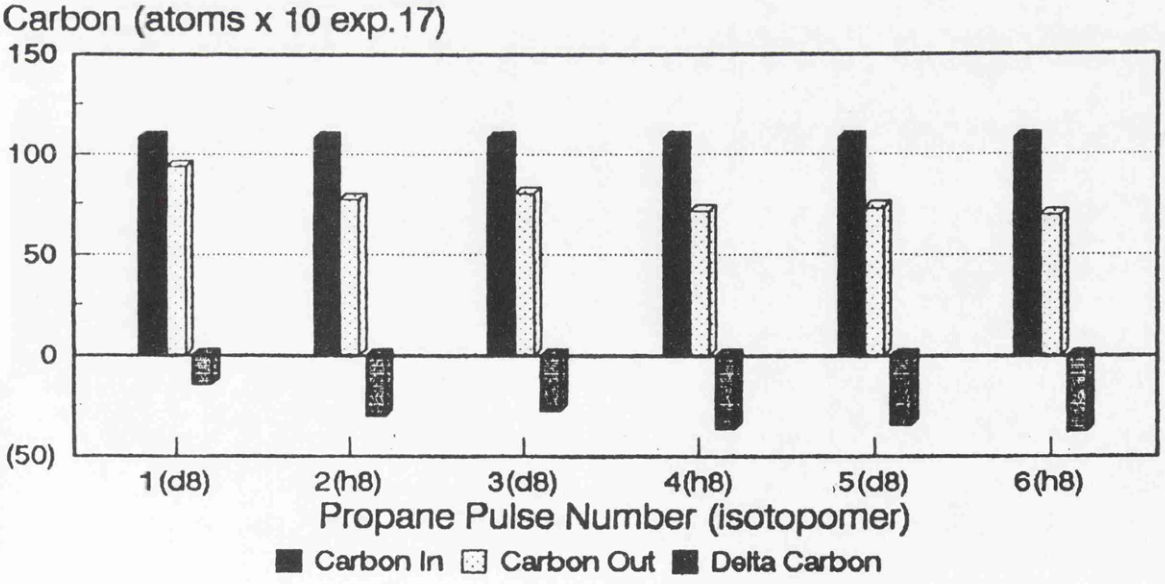


Table 5.4c Hydrogen Balance for the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Pt/alumina Catalyst at 500°C.
(Catalyst weight = 0.2016 g).

Hydrogen atoms x 10^{17}

Pulse	Hydrogen In	Hydrogen Out	Delta Hydrogen
1(C_3D_8)	288.0	184.0	-104.0
2(C_3H_8)	288.0	179.2	-108.8
3(C_3D_8)	288.0	207.6	-80.4
4(C_3H_8)	288.0	183.6	-104.4
5(C_3D_8)	288.0	192.6	-95.4
6(C_3H_8)	288.0	193.6	-94.4

Total hydrogen lost to the catalyst = 587.4 x 10^{17} atoms.

Table 5.4d Ratio of Carbon:Hydrogen Lost to the Catalyst During the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Pt/alumina Catalyst at 500°C.
(Catalyst weight = 0.2016 g).

Pulse	1 (C_3D_8)	2 (C_3H_8)	3 (C_3D_8)	4 (C_3H_8)	5 (C_3D_8)	6 (C_3H_8)	Total
Ratio of C:H Lost to Catalyst	1:4	1:3	1:3	1:3	1:3	1:3	1:3

Figure 5.1c Hydrogen Balance for the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Pt/alumina Catalyst at 500°C. (Catalyst weight = 0.2016 g).

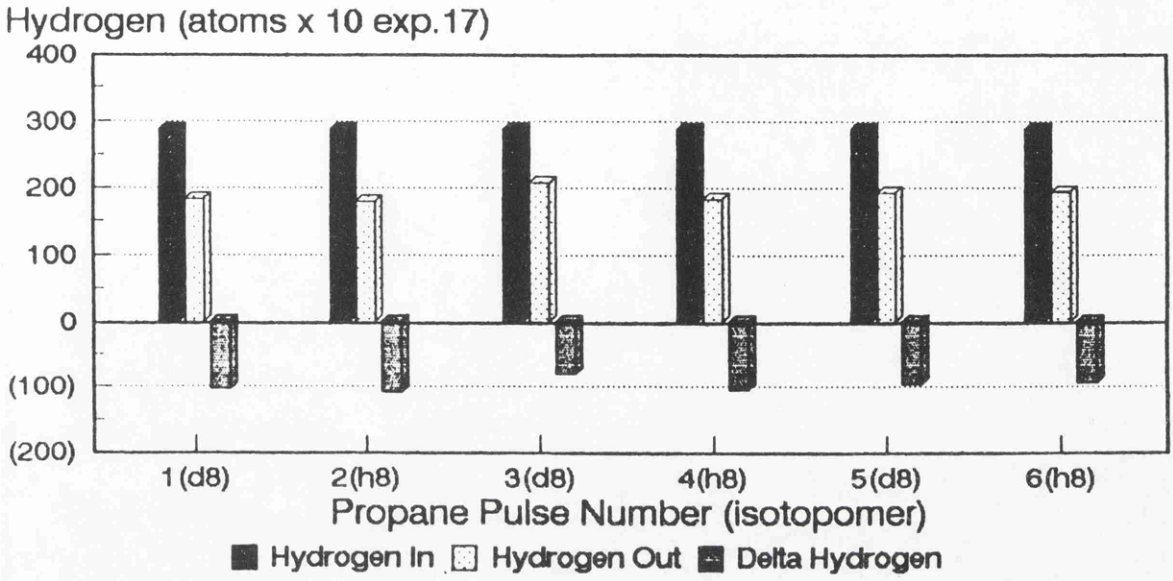


Table 5.4e Oxygen Balance for the Interaction of Dioxygen with the Used Pt/alumina Catalyst at 500°C.
(Catalyst weight =0.2016 g).

Molecules x 10^{17}

Pulse	O_2 In	O_2 Out	CO Out	CO_2 Out	O_2 Taken Up
1(O_2)	36.0	0.0	0.9	30.8	4.8
2(O_2)	36.0	0.0	0.7	29.2	6.4
3(O_2)	36.0	3.0	0.0	21.3	11.7
4(O_2)	36.0	28.1	0.0	2.0	5.9
5(O_2)	36.0	35.7	0.0	0.0	0.3
6(O_2)	36.0	34.1	0.0	0.0	1.9

Total carbon burnt off catalyst as CO or CO_2 = 84.9 x 10^{17} atoms.

Table 5.4f Calculated Ratio of Isotopic Methanes Produced During the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Pt/alumina Catalyst at 500°C.

Pulse	CD_4	CD_3H	CD_2H_2	CDH_3	CH_4
1(C_3D_8)	1	3	12	19	65
2(C_3H_8)	0	2	16	32	50
3(C_3D_8)	1	6	26	36	31
4(C_3H_8)	1	6	27	36	30
5(C_3D_8)	2	12	30	36	20
6(C_3H_8)	2	9	29	36	24

Table 5.4g Normalised Mass Spectra for Unreacted Propane During the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Pt/alumina Catalyst at 500°C.

m/z	Pulse			
	3(C_3D_8)	4(C_3H_8)	5(C_3D_8)	6(C_3H_8)
36	0.00	0.00	1.05	0.10
37	0.00	0.07	0.00	0.30
38	0.00	0.60	0.42	0.45
39	0.00	2.93	1.05	1.20
40	0.00	0.00	0.89	0.05
41	0.60	0.87	1.05	0.40
42	1.83	1.07	2.13	0.70
43	1.20	1.67	0.53	1.50
44	0.00	0.00	0.95	0.00
45	0.60	1.00	0.53	1.00
46	0.75	1.33	1.71	0.60
47	0.00	0.00	0.00	0.00
48	0.00	0.00	0.42	0.00
49	0.00	0.00	1.02	0.00
50	1.00	0.00	1.93	0.00
51	0.00	0.00	1.00	0.00
52	0.00	0.00	0.00	0.00

Experiment PADPR.02

Table 5.5a Product Distribution for the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Pt/alumina Catalyst at 550°C.
(Catalyst weight = 0.2095 g; pulse size = 36.0 x 10^{17} molecules).

Product molecules x 10^{17}

Pulse	CO	CX_4	CO_2
1(C_3D_8)	65.8	26.9	0.7
2(C_3H_8)	44.1	33.0	0.0
3(C_3D_8)	37.9	42.1	0.0
4(C_3H_8)	32.1	39.2	0.0
5(C_3D_8)	29.2	43.6	0.0
6(C_3H_8)	25.8	43.7	0.0

Table 5.5b Carbon Balance for the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Pt/alumina Catalyst at 550°C.
(Catalyst weight = 0.2095 g).

Carbon atoms x 10^{17}

Pulse	Carbon In	Carbon Out	Delta Carbon
1(C_3D_8)	108.0	93.4	-14.6
2(C_3H_8)	108.0	77.1	-30.9
3(C_3D_8)	108.0	80.0	-28.0
4(C_3H_8)	108.0	71.3	-36.7
5(C_3D_8)	108.0	72.8	-35.2
6(C_3H_8)	108.0	69.5	-38.5

Total carbon lost to the catalyst = 183.9 x 10^{17} atoms.

Experiment PADPR.02

Figure 5.2a Product Distribution for the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Pt/alumina Catalyst at 550°C. (Catalyst weight = 0.2095 g; pulse size = 36.0 x 10^{17} molecules).

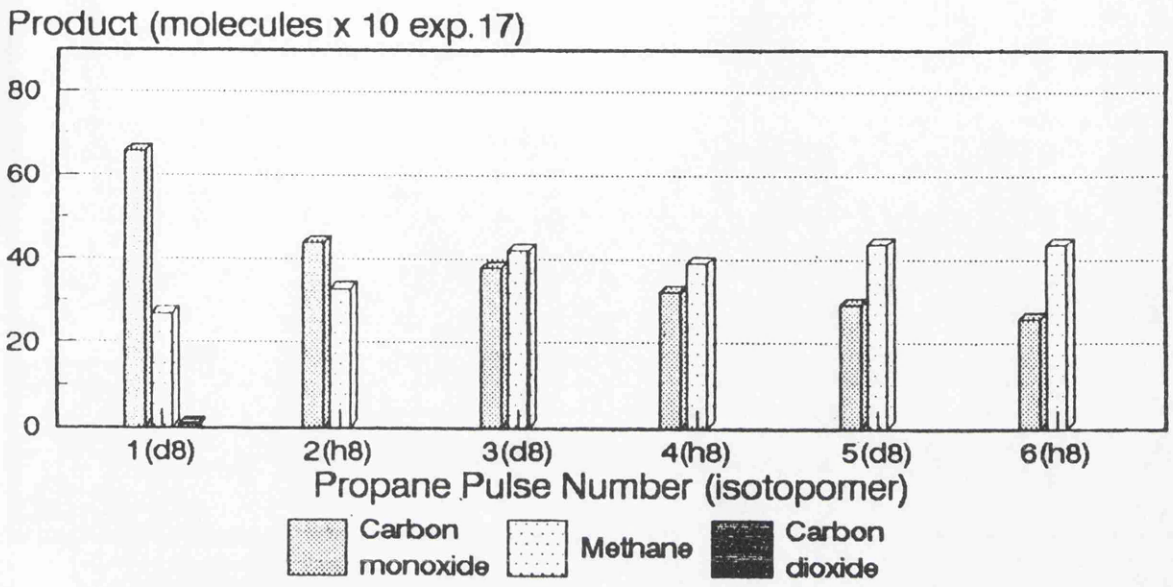


Figure 5.2b Carbon Balance for the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Pt/alumina Catalyst at 550°C. (Catalyst weight = 0.2095 g).

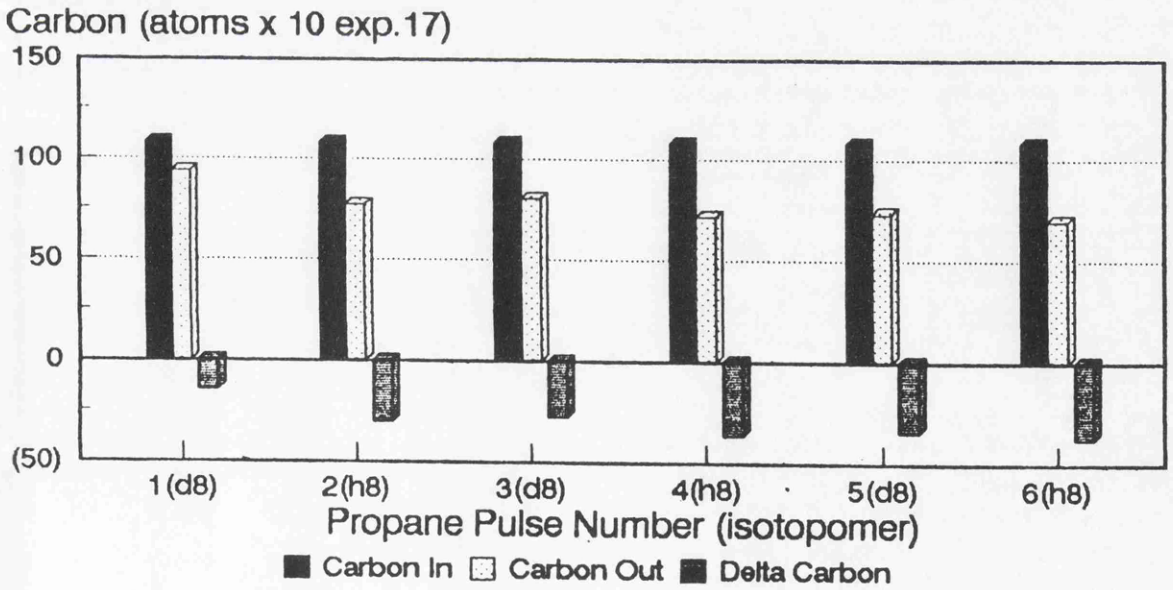


Table 5.5c Hydrogen Balance for the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Pt/alumina Catalyst at 550°C.
(Catalyst weight = 0.2095 g).

Hydrogen atoms x 10^{17}

Pulse	Hydrogen In	Hydrogen Out	Delta Hydrogen
1(C_3D_8)	288.0	107.6	-180.4
2(C_3H_8)	288.0	132.0	-156.0
3(C_3D_8)	288.0	168.4	-119.6
4(C_3H_8)	288.0	156.8	-131.2
5(C_3D_8)	288.0	174.4	-113.6
6(C_3H_8)	288.0	174.8	-113.2

Total hydrogen lost to the catalyst = 814.0 x 10^{17} atoms.

Table 5.5d Ratio of Carbon:Hydrogen Lost to the Catalyst During the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Pt/alumina Catalyst at 550°C.
(Catalyst weight = 0.2095 g).

Pulse	1 (C_3D_8)	2 (C_3H_8)	3 (C_3D_8)	4 (C_3H_8)	5 (C_3D_8)	6 (C_3H_8)	Total
Ratio of C:H Lost to Catalyst	1:12	1:5	1:4	1:4	1:3	1:3	1:4

Figure 5.2c Hydrogen Balance for the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Pt/alumina Catalyst at 550°C. (Catalyst weight = 0.2095 g).

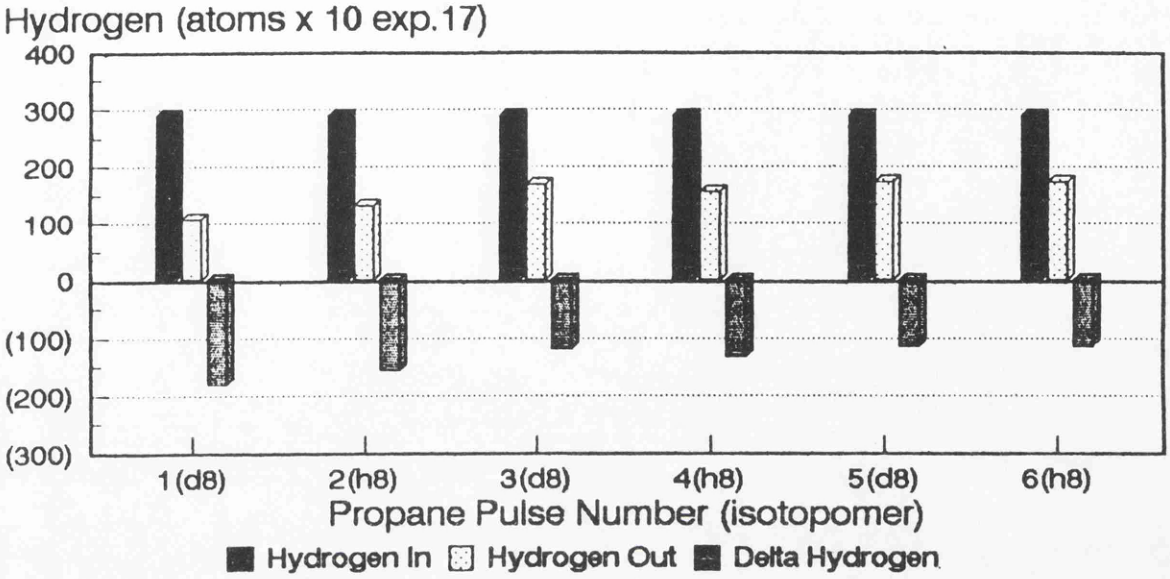


Table 5.5e Oxygen Balance for the Interaction of Dioxygen with the Used Pt/alumina Catalyst at 550°C.
(Catalyst weight = 0.2095 g).

Molecules x 10^{17}

Pulse	O_2 In	O_2 Out	CO Out	CO_2 Out	O_2 Taken Up
1(O_2)	36.0	0.0	0.9	31.8	3.8
2(O_2)	36.0	0.0	0.4	31.7	4.1
3(O_2)	36.0	16.0	0.0	7.4	12.6
4(O_2)	36.0	32.1	0.0	0.0	3.9
5(O_2)	36.0	35.8	0.0	0.0	0.2
6(O_2)	36.0	35.9	0.0	0.0	0.1

Total carbon burnt off catalyst as CO or CO_2 = 72.2 x 10^{17} atoms.

Table 5.5f Calculated Ratio of Isotopic Methanes Produced During the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Pt/alumina Catalyst at 550°C.

Pulse	CD_4	CD_3H	CD_2H_2	CDH_3	CH_4
1(C_3D_8)	2	3	22	14	59
2(C_3H_8)	2	3	24	37	34
3(C_3D_8)	1	3	31	35	36
4(C_3H_8)	3	11	29	37	20
5(C_3D_8)	4	14	32	33	17
6(C_3H_8)	3	14	37	32	14

Experiment PADPR.03

Table 5.6a Product Distribution for the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Pt/alumina Catalyst at 600°C. (Catalyst weight = 0.2170 g; pulse size = 36.0 x 10^{17} molecules).

Product molecules x 10^{17}

Pulse	CO	CX_4	CO_2
1(C_3D_8)	81.4	20.2	0.5
2(C_3H_8)	55.4	23.9	0.0
3(C_3D_8)	39.1	31.7	0.0
4(C_3H_8)	27.9	30.1	0.0
5(C_3D_8)	23.7	36.3	0.0
6(C_3H_8)	18.0	34.0	0.0

Table 5.6b Carbon Balance for the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Pt/alumina Catalyst at 600°C. (Catalyst weight = 0.2170 g).

Carbon atoms x 10^{17}

Pulse	Carbon In	Carbon Out	Delta Carbon
1(C_3D_8)	108.0	102.1	-5.9
2(C_3H_8)	108.0	79.3	-28.7
3(C_3D_8)	108.0	70.8	-37.2
4(C_3H_8)	108.0	58.0	-50.0
5(C_3D_8)	108.0	60.0	-48.0
6(C_3H_8)	108.0	52.0	-56.0

Total carbon lost to the catalyst = 225.8 x 10^{17} atoms.

Experiment PADPR.03

Figure 5.3a Product Distribution for the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Pt/alumina Catalyst at 600°C. (Catalyst weight = 0.2170 g; pulse size = 36.0 x 10^{17} molecules).

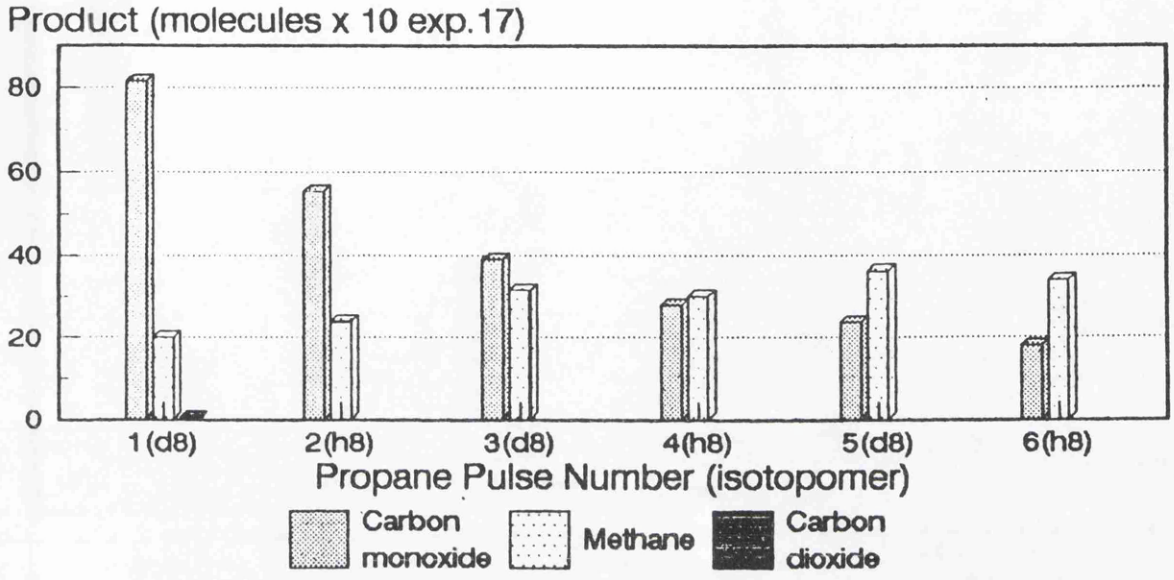


Figure 5.3b Carbon Balance for the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Pt/alumina Catalyst at 600°C. (Catalyst weight = 0.2170 g).

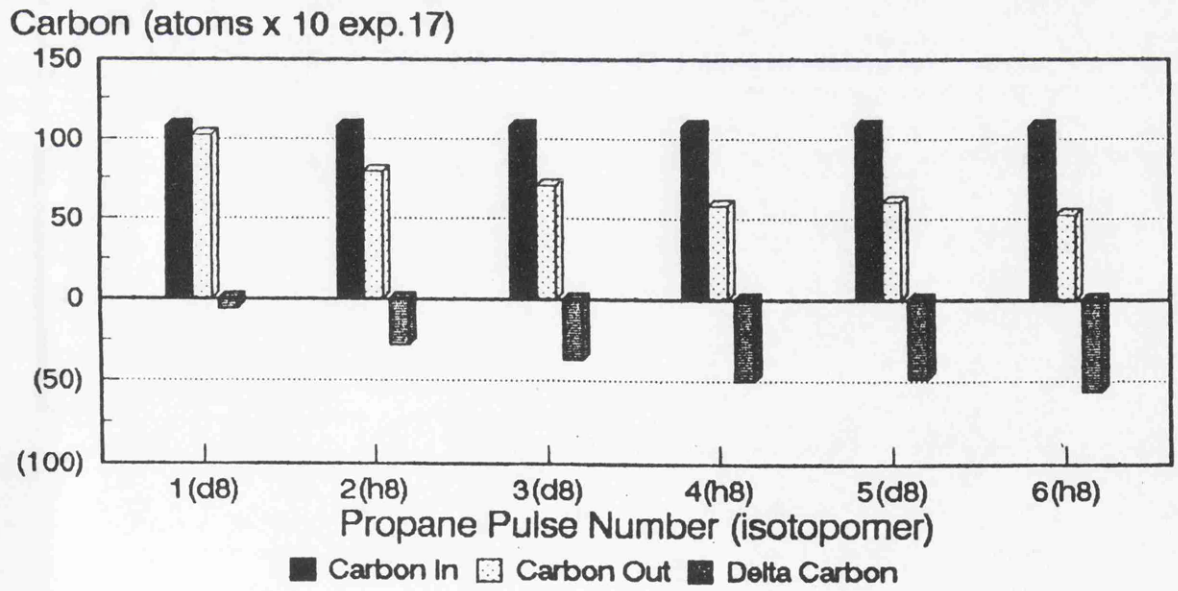


Table 5.6c Hydrogen Balance for the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Pt/alumina Catalyst at 600°C.
(Catalyst weight = 0.2170 g).

Hydrogen atoms x 10^{17}

Pulse	Hydrogen In	Hydrogen Out	Delta Hydrogen
1(C_3D_8)	288.0	80.8	-207.2
2(C_3H_8)	288.0	95.6	-192.4
3(C_3D_8)	288.0	126.8	-161.2
4(C_3H_8)	288.0	120.4	-167.6
5(C_3D_8)	288.0	145.2	-142.8
6(C_3H_8)	288.0	136.0	-152.0

Total hydrogen lost to the catalyst = 1023.2 x 10^{17} atoms.

Table 5.6d Ratio of Carbon:Hydrogen Lost to the Catalyst During the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Pt/alumina Catalyst at 600°C.
(Catalyst weight = 0.2170 g).

Pulse	1 (C_3D_8)	2 (C_3H_8)	3 (C_3D_8)	4 (C_3H_8)	5 (C_3D_8)	6 (C_3H_8)	Total
Ratio of C:H Lost to Catalyst	1:34	1:7	1:4	1:3	1:3	1:3	1:4

Figure 5.3c Hydrogen Balance for the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Pt/alumina Catalyst at 600°C. (Catalyst weight = 0.2170 g).

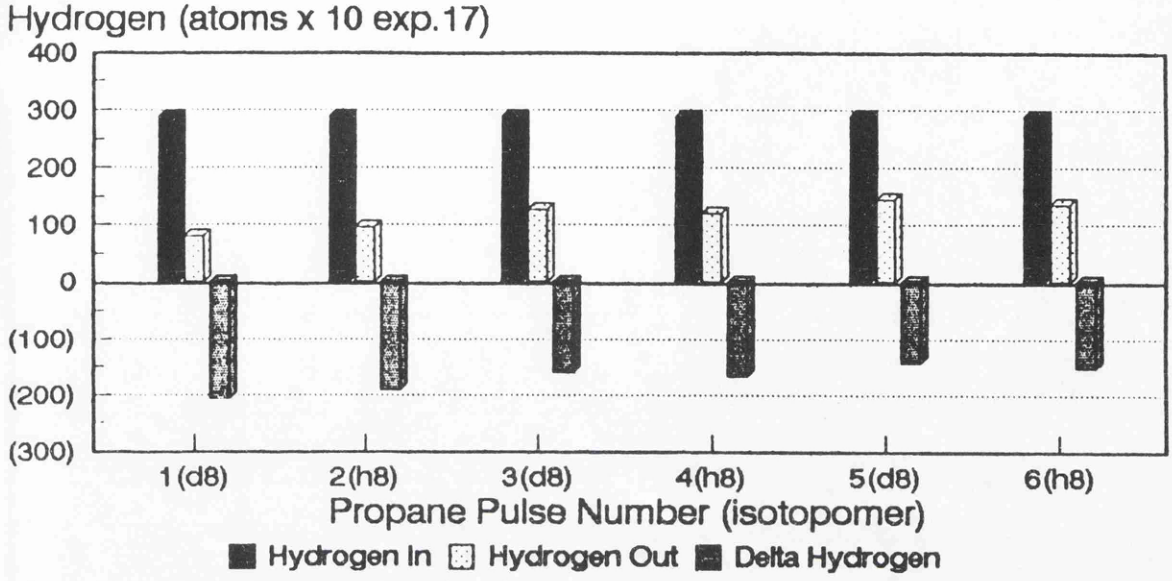


Table 5.6e Oxygen Balance for the Interaction of Dioxygen with the Used Pt/alumina Catalyst at 600°C.
(Catalyst weight 0.2170 g).

Molecules x 10^{17}

Pulse	O_2 In	O_2 Out	CO Out	CO_2 Out	O_2 Taken Up
1(O_2)	36.0	0.0	7.1	23.4	9.0
2(O_2)	36.0	0.0	5.3	20.5	12.8
3(O_2)	36.0	33.5	0.0	1.2	1.3
4(O_2)	36.0	36.0	0.0	trace	0.0
5(O_2)	36.0	34.6	0.0	0.0	1.4
6(O_2)	36.0	35.1	0.0	0.0	0.9

Total carbon burnt off catalyst as CO or CO_2 = 57.5 x 10^{17} atoms.

Table 5.6f Calculated Ratio of Isotopic Methanes Produced During the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Pt/alumina Catalyst at 600°C.

Pulse	CD_4	CD_3H	CD_2H_2	CDH_3	CH_4
1(C_3D_8)	2	12	42	22	22
2(C_3H_8)	2	15	45	22	16
3(C_3D_8)	3	16	40	25	16
4(C_3H_8)	3	19	42	24	12
5(C_3D_8)	4	19	40	26	11
6(C_3H_8)	5	22	44	21	8

Experiment PACPR.11

Table 5.7a Product Distribution for the Interaction of Pulses of (2-^{13}C)-C_3H_8 and C_3H_8 with a Pt/alumina Catalyst at 600°C.
(Weight of Catalyst = 0.2105 g; pulse size = 36.0 x 10^{17} molecules).

Product molecules x 10^{17}

Pulse	CO	CX_4	CO_2
1((2-^{13}C)-C_3H_8)	63.8	34.9	2.7
2(C_3H_8)	58.9	40.5	2.7
3(C_3H_8)	57.8	39.1	1.7
4((2-^{13}C)-C_3H_8)	56.0	41.3	1.7
5((2-^{13}C)-C_3H_8)	57.7	40.2	0.9
6(C_3H_8)	55.9	44.1	0.9
7(C_3H_8)	52.2	42.5	0.8

Table 5.7b Carbon Balance for the Interaction of Pulses of (2-^{13}C)-C_3H_8 and C_3H_8 with a Pt/alumina Catalyst at 600°C.
(Catalyst weight = 0.2105 g).

Carbon atoms x 10^{17}

Pulse	Carbon In	Carbon Out	Delta Carbon
1((2-^{13}C)-C_3H_8)	108.0	101.4	-6.6
2(C_3H_8)	108.0	102.1	-5.9
3(C_3H_8)	108.0	98.6	-9.4
4((2-^{13}C)-C_3H_8)	108.0	99.0	-9.0
5((2-^{13}C)-C_3H_8)	108.0	98.8	-9.2
6(C_3H_8)	108.0	100.9	-7.1
7(C_3H_8)	108.0	95.5	-12.5

Total carbon lost to the catalyst = 59.7 x 10^{17} atoms.

Experiment PACPR.11

Figure 5.4a Product Distribution for the Interaction of Pulses of (2-^{13}C)-C_3H_8 and C_3H_8 with a Pt/alumina Catalyst at 600°C. (Weight of Catalyst = 0.2105 g; pulse size = 36.0 x 10^{17} molecules).

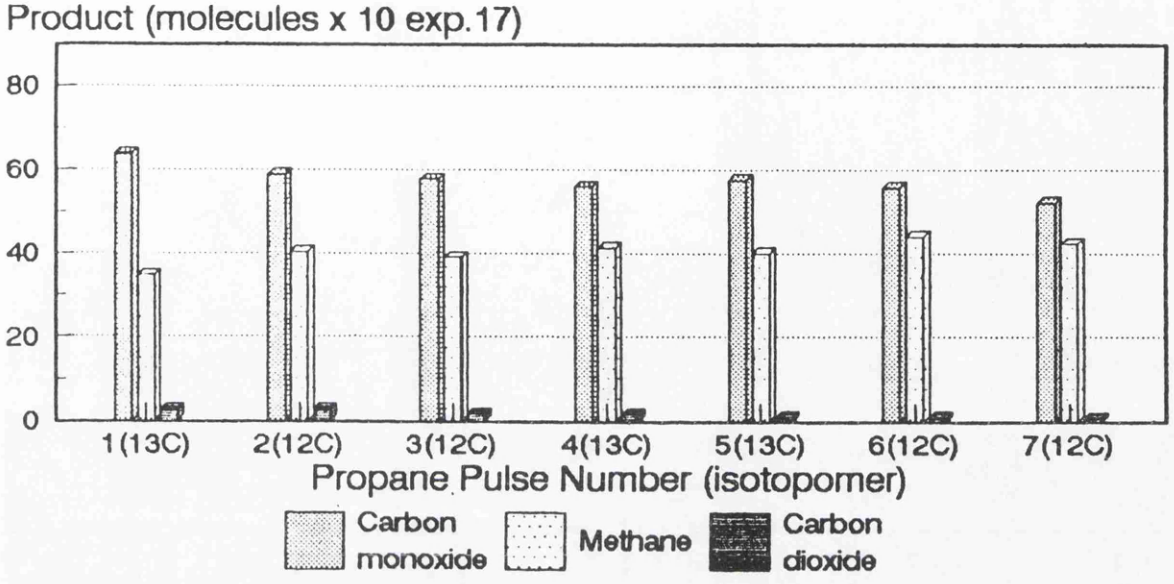


Figure 5.4b Carbon Balance for the Interaction of Pulses of (2-^{13}C)-C_3H_8 and C_3H_8 with a Pt/alumina Catalyst at 600°C. (Catalyst weight = 0.2105 g).

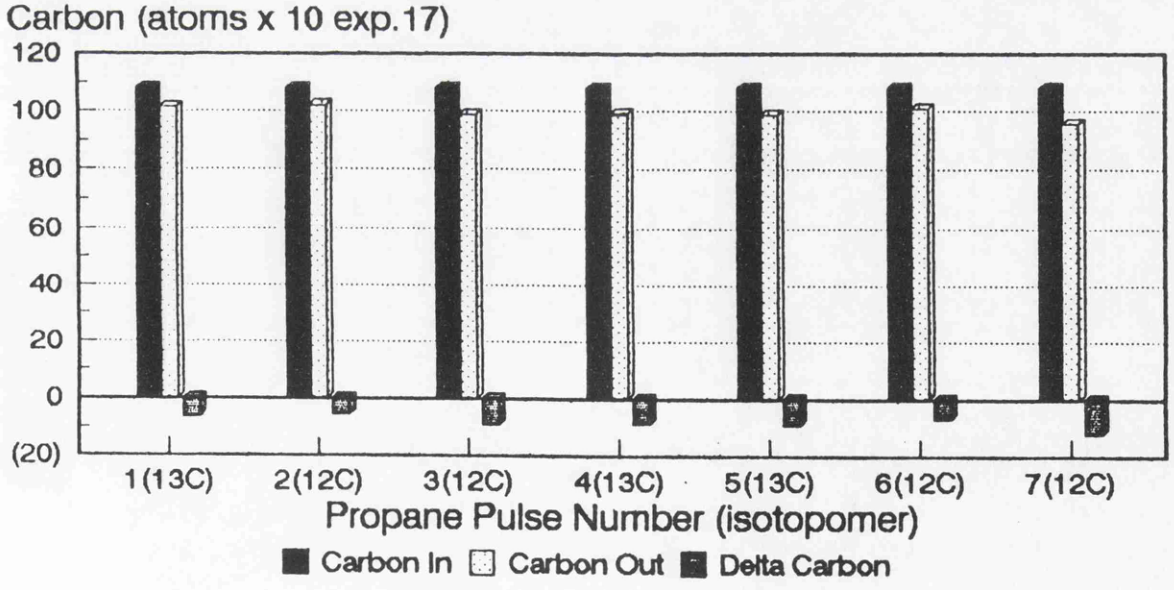


Table 5.7c Hydrogen Balance for the Interaction of Pulses of (2-^{13}C)-C_3H_8 and C_3H_8 with a Pt/alumina Catalyst at 600°C.
(Catalyst weight = 0.2105 g).

Hydrogen atoms x 10^{17}

Pulse	Hydrogen In	Hydrogen Out	Delta Hydrogen
1((2-^{13}C)-C_3H_8)	288.0	139.6	-148.4
2(C_3H_8)	288.0	162.0	-126.0
3(C_3H_8)	288.0	156.4	-131.6
4((2-^{13}C)-C_3H_8)	288.0	165.2	-122.8
5((2-^{13}C)-C_3H_8)	288.0	160.8	-127.2
6(C_3H_8)	288.0	176.4	-111.6
7(C_3H_8)	288.0	170.0	-118.0

Total hydrogen lost to the catalyst = 885.6 x 10^{17} atoms.

Table 5.7d Ratio of Carbon:Hydrogen Lost to the Catalyst During the Interaction of Pulses of (2-^{13}C)-C_3H_8 and C_3H_8 with a Pt/alumina Catalyst at 600°C.
(Catalyst weight = 0.2105 g).

Pulse	1 (^{13}C)	2	3	4 (^{13}C)	5 (^{13}C)	6	7	Total
Ratio of C:H Lost to Catalyst	1:21	1:21	1:15	1:14	1:14	1:16	1:10	1:15

Figure 5.4c Hydrogen Balance for the Interaction of Pulses of (2-^{13}C)-C_3H_8 and C_3H_8 with a Pt/alumina Catalyst at 600°C. (Catalyst weight = 0.2105 g).

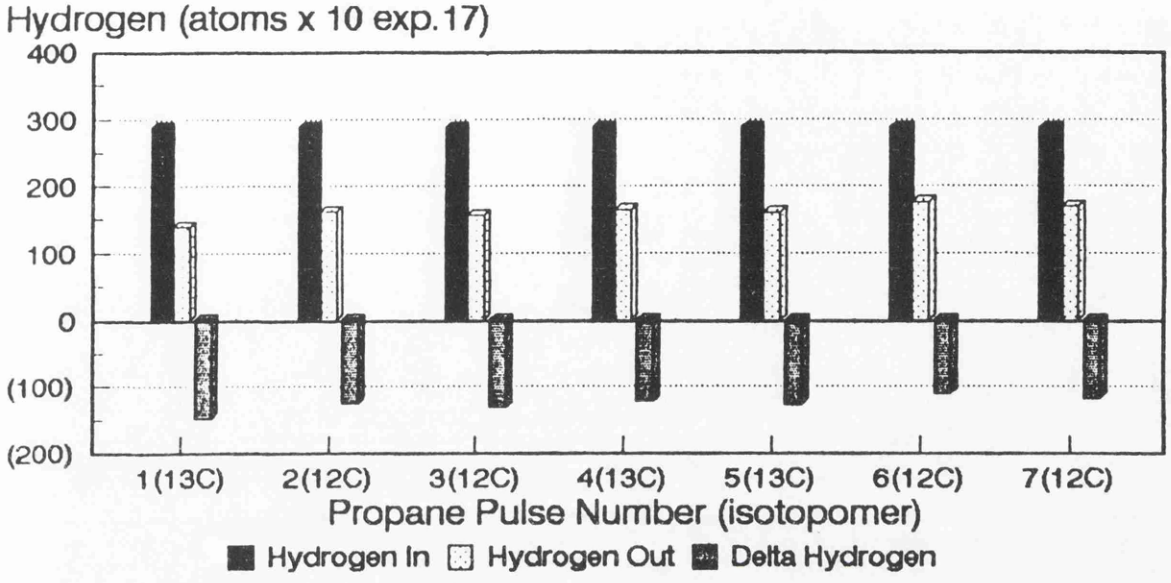


Table 5.7e Ratio of ^{12}C:^{13}C in the Products from the Interaction of Pulses of (2-^{13}C)-C_3H_8 and C_3H_8 with a Pt/alumina Catalyst at 600°C.

Pulse	$^{12}CO_2$:$^{13}CO_2$	^{12}CO:^{13}CO	$^{12}CH_4$:$^{13}CH_4$
1((2-^{13}C)-C_3H_8)	1:1	2:1	2:1
2(C_3H_8)	∞[a]	∞[a]	∞[a]
3(C_3H_8)	∞[a]	∞[a]	∞[a]
4((2-^{13}C)-C_3H_8)	1:1	2:1	2:1
5((2-^{13}C)-C_3H_8)	1:1	2:1	2:1
6(C_3H_8)	∞[a]	∞[a]	∞[a]
7(C_3H_8)	∞[a]	∞[a]	∞[a]

[a] ∞ means that only ^{12}C was observed.

Experiment CADPR.11

Table 5.8a Product Distribution for the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Chromia/alumina Catalyst at 500°C. (Catalyst weight =0.1876 g; pulse size = 36.0 x 10^{17} molecules).

Product molecules x 10^{17}

Pulse	CO	CX_4	CO_2	C_2X_6	C_3X_6	C_3X_8
1(C_3D_8)	0.9	0.2	0.2	0.0	0.0	33.5
2(C_3H_8)	1.2	0.2	0.1	trace	9.3	22.9
3(C_3D_8)	1.0	0.2	0.4	trace	0.0	34.4
4(C_3H_8)	1.4	0.2	0.3	trace	10.2	23.0
5(C_3D_8)	0.8	0.1	0.4	0.0	0.0	34.8
6(C_3H_8)	2.0	0.2	0.7	trace	10.7	21.0

Table 5.8b Carbon Balance for the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Chromia/alumina Catalyst at 500°C. (Catalyst weight = 0.1876 g).

Carbon atoms x 10^{17}

Pulse	Carbon In	Carbon Out	Delta Carbon
1(C_3D_8)	108.0	101.8	-6.2
2(C_3H_8)	108.0	98.1	-9.9
3(C_3D_8)	108.0	104.8	-3.2
4(C_3H_8)	108.0	101.5	-6.5
5(C_3D_8)	108.0	105.7	-2.3
6(C_3H_8)	108.0	98.0	-10.0

Total carbon lost to the catalyst = 38.1 x 10^{17} atoms.

Experiment CADPR.11

Figure 5.5a Product Distribution for the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Chromia/alumina Catalyst at 500°C. (Catalyst weight =0.1876 g; pulse size = 36.0 x 10^{17} molecules).

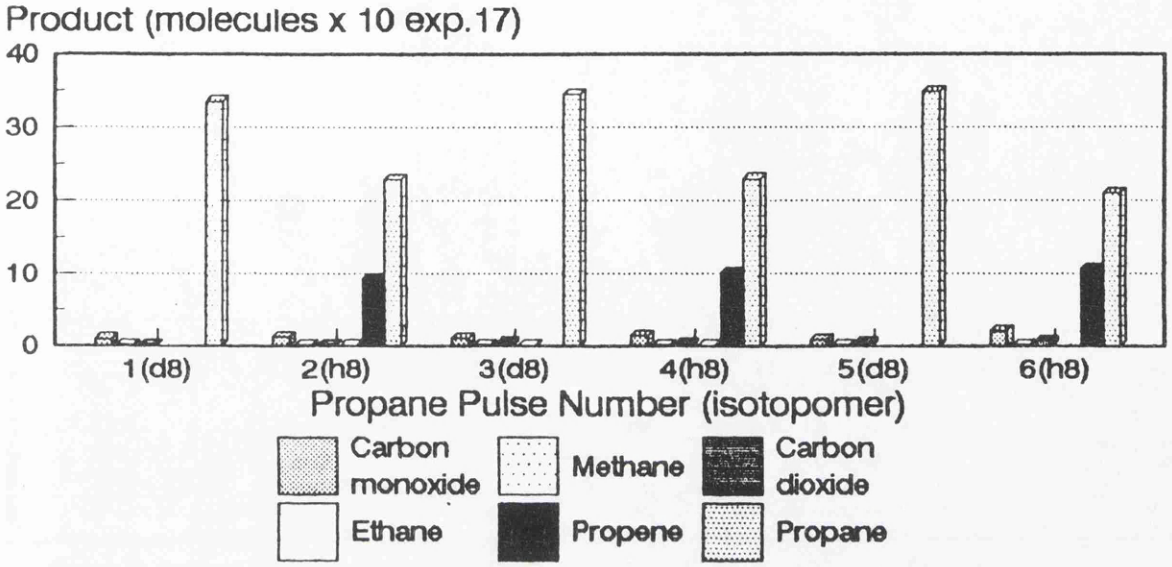


Figure 5.5b Carbon Balance for the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Chromia/alumina Catalyst at 500°C. (Catalyst weight = 0.1876 g).

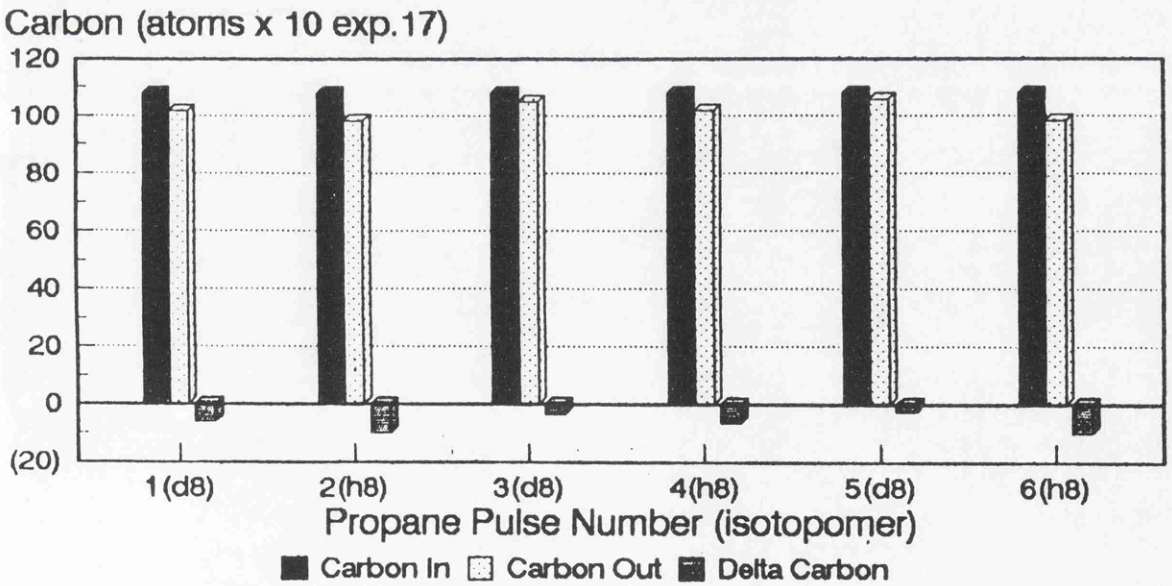


Table 5.8c Hydrogen Balance for the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Chromia/alumina Catalyst at 500°C. (Catalyst weight = 0.1876 g).

Hydrogen atoms x 10^{17}

Pulse	Hydrogen In	Hydrogen Out	Delta Hydrogen
1(C_3D_8)	288.0	268.8	-19.2
2(C_3H_8)	288.0	239.8	-48.2
3(C_3D_8)	288.0	276.0	-12.0
4(C_3H_8)	288.0	246.0	-42.0
5(C_3D_8)	288.0	278.8	-9.2
6(C_3H_8)	288.0	233.0	-55.0

Total hydrogen lost to the catalyst = 185.6 x 10^{17} atoms.

Table 5.8d Ratio of Carbon:Hydrogen Lost to the Catalyst During the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Chromia/alumina Catalyst at 500°C. (Catalyst weight = 0.1876 g).

Pulse	1 (C_3D_8)	2 (C_3H_8)	3 (C_3D_8)	4 (C_3H_8)	5 (C_3D_8)	6 (C_3H_8)	Total
Ratio of C:H Lost to Catalyst	1:3	1:5	1:4	1:7	1:4	1:6	1:5

Figure 5.5c Hydrogen Balance for the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Chromia/alumina Catalyst at 500°C. (Catalyst weight = 0.1876 g).

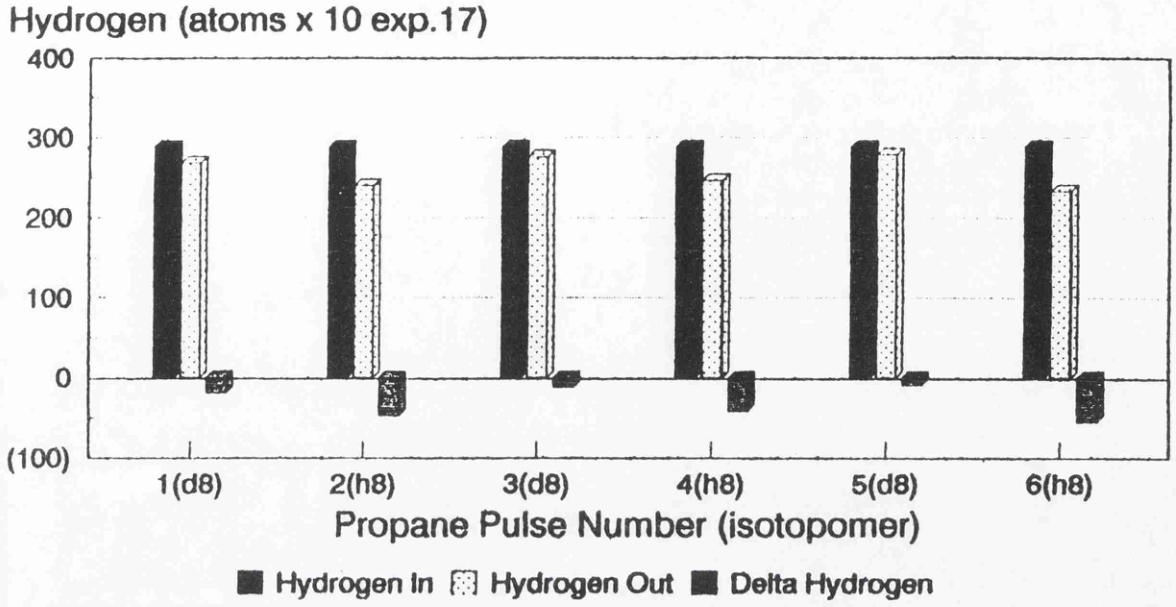


Table 5.8e Oxygen Balance for the Interaction of Dioxygen with the Used Chromia/alumina Catalyst at 500°C.
(Catalyst weight = 0.1876 g).

Molecules x 10^{17}

Pulse	O_2 In	O_2 Out	CO Out	CO_2 Out	O_2 Taken Up
1(O_2)	36.0	0.0	0.2	2.9	33.0
2(O_2)	36.0	0.0	0.1	2.1	33.8
3(O_2)	36.0	0.5	0.0	1.5	34.0
4(O_2)	36.0	0.5	0.0	1.3	34.2
5(O_2)	36.0	1.1	0.0	1.3	33.6
6(O_2)	36.0	4.2	0.0	0.9	30.9
7(O_2)	36.0	7.0	0.0	0.4	28.6
8(O_2)	36.0	12.5	0.0	0.3	23.2
9(O_2)	36.0	19.0	0.0	0.0	17.0
10(O_2)	36.0	25.3	0.0	0.0	10.7

Total carbon burnt off catalyst as CO or CO_2 = 11.0 x 10^{17} atoms.

Table 5.8f Normalised Mass Spectra for Propene Produced During the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Chromia/alumina Catalyst at 500°C.

m/z	Pulse 1 C_3D_8	Pulse 2 C_3H_8	Pulse 3 C_3D_8	Pulse 4 C_3H_8	Pulse 5 C_3D_8	Pulse 6 C_3H_8
36	0.00	0.03	0.00	0.00	0.00	0.04
37	0.00	0.28	0.00	0.21	0.00	0.33
38	0.00	0.39	0.00	0.26	0.00	0.30
39	0.00	1.10	0.00	1.18	0.00	1.36
40	0.00	0.29	0.00	0.13	0.00	0.42
41	0.00	1.00	0.00	1.00	0.00	1.00
42	0.00	0.60	0.00	0.57	0.00	1.05
43	0.00	0.85	0.00	0.88	0.00	0.92
44	0.00	0.00	0.00	0.00	0.00	0.00
45	0.00	0.06	0.00	0.01	0.00	0.00

Table 5.8g Normalised Mass Spectra for Unreacted Propane During the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Chromia/alumina Catalyst at 500°C.

m/z	Pulse 1 C_3D_8	Pulse 2 C_3H_8	Pulse 3 C_3D_8	Pulse 4 C_3H_8	Pulse 5 C_3D_8	Pulse 6 C_3H_8
36	0.00	0.00	0.00	0.00	0.20	0.06
37	0.00	0.33	0.00	0.21	0.30	0.35
38	1.00	0.47	0.54	0.29	0.60	0.35
39	1.00	1.27	0.69	1.21	1.10	1.47
40	0.00	0.33	1.38	0.14	1.40	0.47
41	0.00	1.13	1.00	1.14	0.80	1.06
42	0.52	0.67	1.46	0.64	1.60	1.12
43	0.00	1.00	0.15	1.00	1.40	1.00
44	0.00	0.00	0.00	0.00	0.00	0.00
45	0.00	0.07	0.08	0.00	0.30	0.00
46	0.00	0.00	0.15	0.00	0.20	0.00
47	0.00	0.00	0.00	0.00	0.30	0.00
48	0.00	0.00	0.15	0.00	0.40	0.00
49	1.00	0.00	0.77	0.00	0.60	0.00
50	0.90	0.00	0.38	0.00	0.10	0.00
51	1.00	0.00	1.00	0.00	1.00	0.00
52	0.00	0.00	0.00	0.00	0.00	0.00

Experiment C(K)ADPR.11

Table 5.9a Product Distribution for the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Chromia/K/alumina Catalyst at 500°C. (Catalyst weight = 0.2108 g; pulse size = 36.0 x 10^{17} molecules).

Product molecules x 10^{17}

Pulse	CO	CX_4	CO_2	C_2X_6	C_3X_6	C_3X_8
1(C_3D_8)	0.9	0.1	1.6	0.0	0.0	32.9
2(C_3H_8)	1.2	0.3	1.6	trace	9.1	22.1
3(C_3D_8)	0.9	0.1	1.6	0.0	0.0	33.3
4(C_3H_8)	1.3	0.2	1.6	trace	11.0	19.3
5(C_3D_8)	1.1	trace	1.7	0.0	0.0	33.9
6(C_3H_8)	1.5	0.2	1.7	0.0	8.6	22.1

Table 5.9b Carbon Balance for the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Chromia/K/alumina Catalyst at 500°C. (Catalyst weight = 0.2108 g).

Carbon atoms x 10^{17}

Pulse	Carbon In	Carbon Out	Delta Carbon
1(C_3D_8)	108.0	101.3	-6.7
2(C_3H_8)	108.0	96.7	-11.3
3(C_3D_8)	108.0	102.5	-5.5
4(C_3H_8)	108.0	94.0	-14.0
5(C_3D_8)	108.0	104.5	-3.5
6(C_3H_8)	108.0	95.5	-12.5

Total carbon lost to the catalyst = 53.5 x 10^{17} atoms.

Experiment C(K)ADPR.11

Figure 5.6a Product Distribution for the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Chromia/K/alumina Catalyst at 500°C. (Catalyst weight = 0.2108 g; pulse size = 36.0 x 10^{17} molecules).

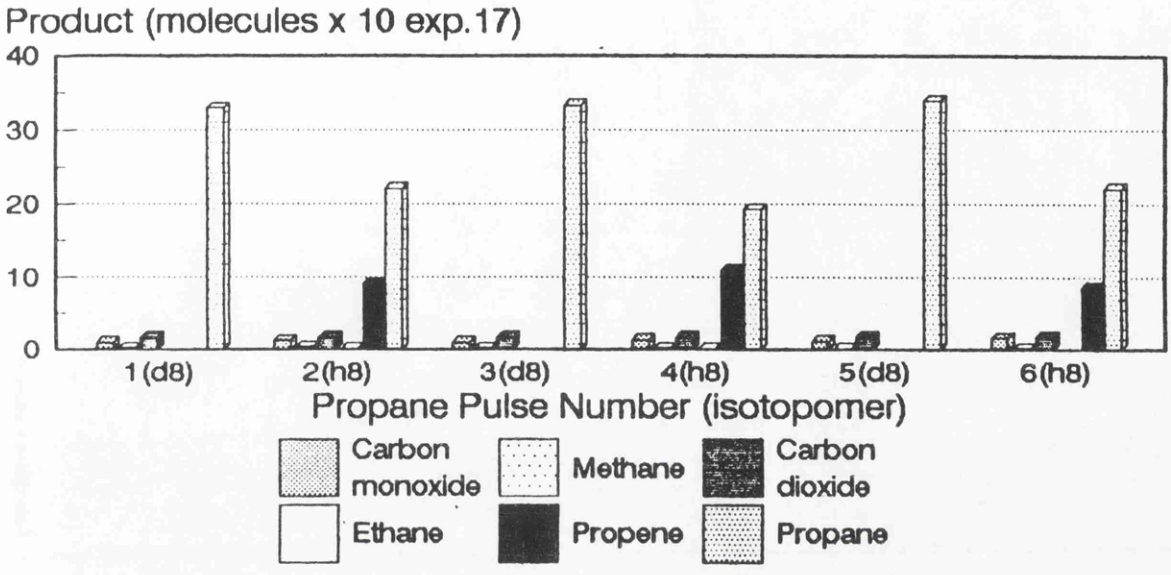


Figure 5.6b Carbon Balance for the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Chromia/K/alumina Catalyst at 500°C. (Catalyst weight = 0.2108 g).

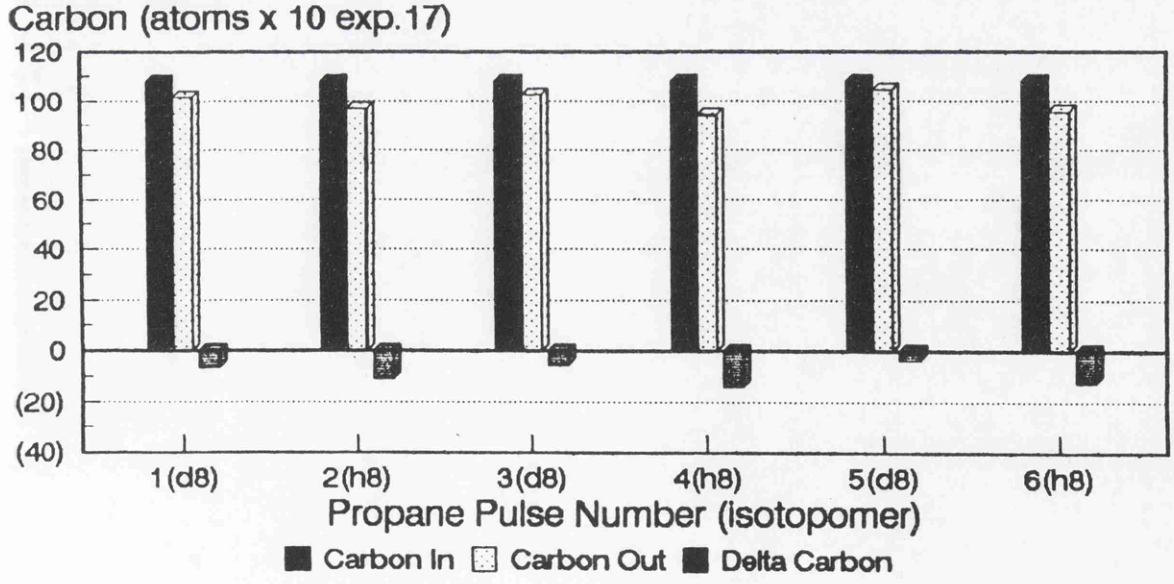


Table 5.9c Hydrogen Balance for the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Chromia/K/alumina Catalyst at 500°C. (Catalyst weight = 0.2108 g).

Hydrogen atoms x 10^{17}

Pulse	Hydrogen In	Hydrogen Out	Delta Hydrogen
1(C_3D_8)	288.0	263.6	-24.4
2(C_3H_8)	288.0	232.6	-55.4
3(C_3D_8)	288.0	266.8	-21.2
4(C_3H_8)	288.0	221.2	-66.8
5(C_3D_8)	288.0	271.2	-16.8
6(C_3H_8)	288.0	229.2	-58.8

Total hydrogen lost to the catalyst = 243.4 x 10^{17} atoms.

Table 5.9d Ratio of Carbon:Hydrogen Lost to the Catalyst During the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Chromia/K/alumina Catalyst at 500°C. (Catalyst weight = 0.2108 g).

Pulse	1 (C_3D_8)	2 (C_3H_8)	3 (C_3D_8)	4 (C_3H_8)	5 (C_3D_8)	6 (C_3H_8)	Total
Ratio of C:H Lost to Catalyst	1:3	1:5	1:4	1:5	1:4	1:5	1:4

Figure 5.6c Hydrogen Balance for the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Chromia/K/alumina Catalyst at 500°C. (Catalyst weight = 0.2108 g).

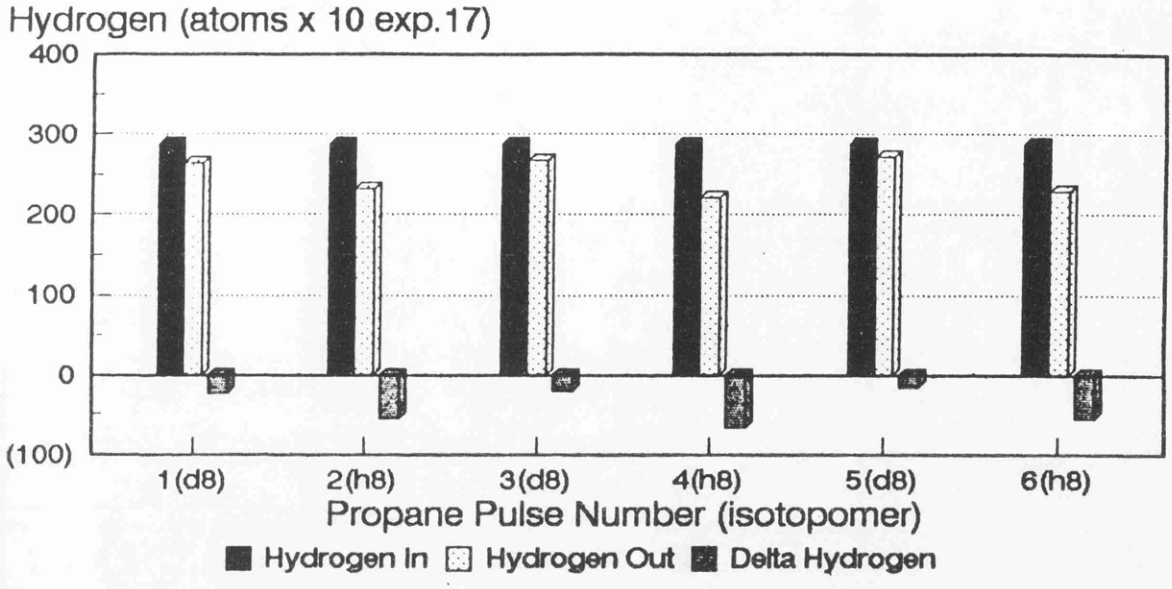


Table 5.9e Oxygen Balance for the Interaction of Dioxygen with the Used Chromia/K/alumina Catalyst at 500°C.

Molecules x 10^{17}

Pulse	O_2 In	O_2 Out	CO Out	CO_2 Out	O_2 Taken Up
1(O_2)	36.0	0.5	0.0	1.4	34.1
2(O_2)	36.0	0.5	0.0	0.7	34.8
3(O_2)	36.0	0.6	0.0	0.5	34.9
4(O_2)	36.0	0.6	0.0	0.4	35.0
5(O_2)	36.0	1.0	0.0	0.3	34.7
6(O_2)	36.0	2.5	0.0	0.2	33.3
7(O_2)	36.0	3.8	0.0	0.1	32.1
8(O_2)	36.0	7.4	0.0	0.1	28.5
9(O_2)	36.0	13.1	0.0	0.0	22.9
10(O_2)	36.0	13.9	0.0	0.0	22.1

Total carbon burnt off catalyst as CO or CO_2 = 3.7 x 10^{17} atoms.

Table 5.9f Normalised Mass Spectra for Propene Produced During the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Chromia/K/alumina Catalyst at 500°C.

m/z	Pulse 1 C_3D_8	Pulse 2 C_3H_8	Pulse 3 C_3D_8	Pulse 4 C_3H_8	Pulse 5 C_3D_8	Pulse 6 C_3H_8
36	0.00	0.00	0.00	0.00	0.00	0.03
37	0.00	0.18	0.00	0.22	0.00	0.25
38	0.00	0.32	0.00	0.37	0.00	0.38
39	0.00	1.12	0.00	1.33	0.00	1.12
40	0.00	0.21	0.00	0.33	0.00	0.28
41	0.00	1.00	0.00	1.00	0.00	1.00
42	0.00	0.56	0.00	0.63	0.00	0.62
43	0.00	0.38	0.00	1.04	0.00	0.97
44	0.00	0.50	0.00	0.67	0.00	0.69
45	0.00	0.00	0.00	0.00	0.00	0.06
46	0.00	0.00	0.00	0.00	0.00	0.00
47	0.00	0.0	0.00	0.00	0.00	0.00
48	0.00	0.00	0.00	0.00	0.00	0.00
49	0.00	0.00	0.00	0.00	0.00	0.00
50	0.00	0.00	0.00	0.00	0.00	0.00
51	0.00	0.00	0.00	0.00	0.00	0.00
52	0.00	0.00	0.00	0.00	0.00	0.00

Table 5.9g Normalised Mass Spectra for Unreacted Propane During the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Chromia/K/alumina Catalyst at 500°C.

m/z	Pulse 1 C_3D_8	Pulse 2 C_3H_8	Pulse 3 C_3D_8	Pulse 4 C_3H_8	Pulse 5 C_3D_8	Pulse 6 C_3H_8
36	0.00	0.00	0.00	0.00	0.00	0.00
37	0.09	0.19	0.08	0.20	0.00	0.25
38	1.46	0.25	0.92	0.30	1.00	0.47
39	1.55	1.59	1.18	0.17	0.55	1.44
40	2.09	0.14	2.30	0.61	2.55	0.28
41	2.55	1.32	1.56	1.48	1.45	1.26
42	4.18	0.75	3.27	1.20	3.16	0.97
43	1.18	1.00	0.90	1.00	1.09	1.00
44	0.00	0.00	0.00	0.00	2.73	0.00
45	0.09	0.02	0.20	0.00	0.18	0.15
46	0.59	0.00	0.27	0.00	0.32	0.08
47	0.00	0.00	0.00	0.00	0.00	0.12
48	0.05	0.00	0.00	0.00	0.00	0.16
49	0.73	0.00	0.41	0.00	0.36	0.04
50	0.31	0.00	0.13	0.05	0.55	0.04
51	1.00	0.00	1.00	0.14	1.00	0.18
52	0.00	0.00	0.00	0.00	0.00	0.14

Experiment C(K)ADPR.12

Table 5.10a Product Distribution for the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Chromia/K/alumina Catalyst at 550°C. (Catalyst weight = 0.2164 g; pulse size = 36.0 x 10^{17} molecules).

Product molecules x 10^{17}

Pulse	CO	CX_4	CO_2	C_2X_6	C_3X_6	C_3X_8
1(C_3D_8)	3.5	0.4	12.2	0.7	8.5	15.2
2(C_3H_8)	3.3	0.5	2.2	0.4	11.9	14.6
3(C_3D_8)	2.3	0.5	1.8	0.3	9.5	22.4
4(C_3H_8)	3.0	0.5	1.5	0.5	12.6	15.6
5(C_3D_8)	2.9	0.4	2.4	0.4	9.8	22.3
6(C_3H_8)	3.2	0.5	1.8	0.4	12.6	15.7

Table 5.10b Carbon Balance for the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Chromia/K/alumina Catalyst at 550°C. (Catalyst weight = 0.2164 g).

Carbon atoms x 10^{17}

Pulse	Carbon In	Carbon Out	Delta Carbon
1(C_3D_8)	108.0	88.6	-19.4
2(C_3H_8)	108.0	86.3	-21.7
3(C_3D_8)	108.0	100.9	-7.1
4(C_3H_8)	108.0	90.6	-17.4
5(C_3D_8)	108.0	102.8	-5.2
6(C_3H_8)	108.0	91.2	-16.8

Total carbon lost to the catalyst = 87.6 x 10^{17} atoms.

Experiment C(K)ADPR.12

Figure 5.7a Product Distribution for the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Chromia/K/alumina Catalyst at 550°C. (Catalyst weight = 0.2164 g; pulse size = 36.0×10^{17} molecules).

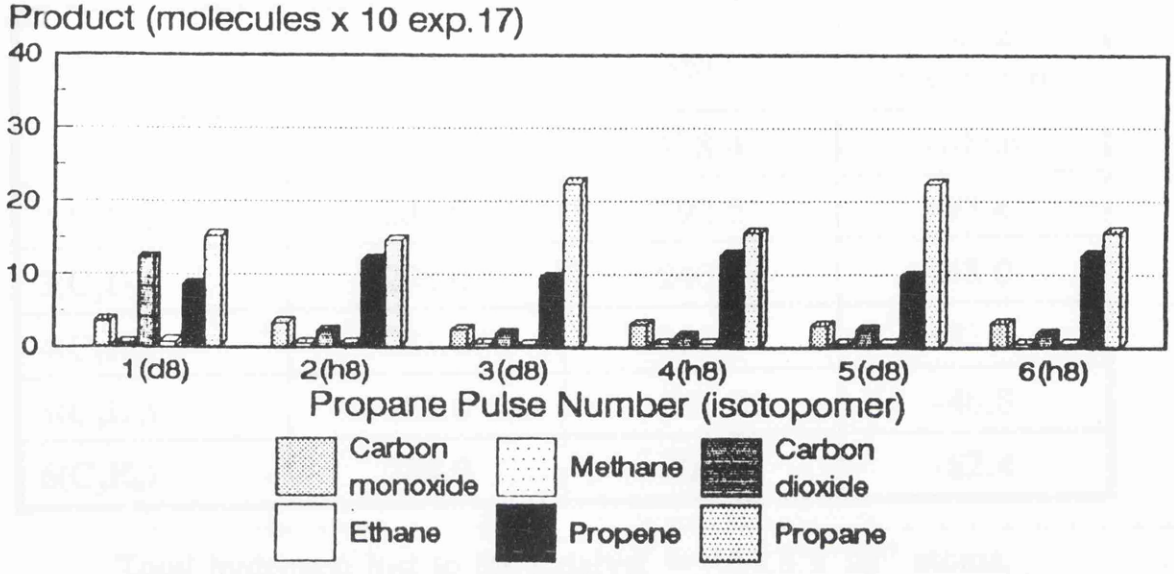


Figure 5.7b Carbon Balance for the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Chromia/K/alumina Catalyst at 550°C. (Catalyst weight = 0.2164 g).

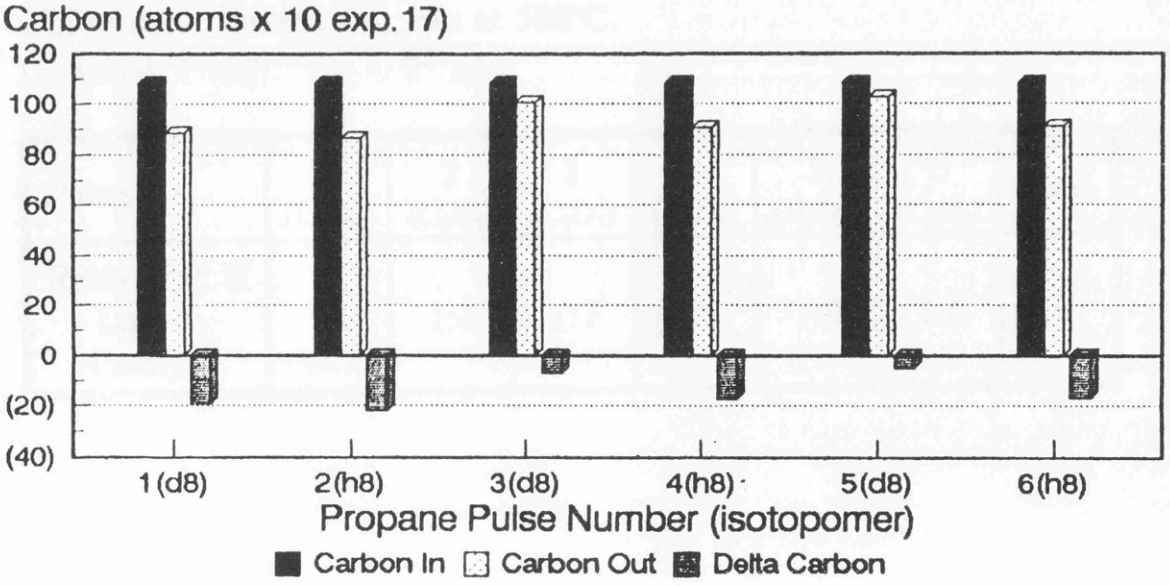


Table 5.10c Hydrogen Balance for the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Chromia/K/alumina Catalyst at 550°C. (Catalyst weight = 0.2164 g).

Hydrogen atoms x 10^{17}

Pulse	Hydrogen In	Hydrogen Out	Delta Hydrogen
1(C_3D_8)	288.0	178.4	-109.6
2(C_3H_8)	288.0	192.6	-95.4
3(C_3D_8)	288.0	240.0	-48.0
4(C_3H_8)	288.0	205.4	-82.6
5(C_3D_8)	288.0	241.2	-46.8
6(C_3H_8)	288.0	205.6	-82.4

Total hydrogen lost to the catalyst = 464.8 x 10^{17} atoms.

Table 5.10d Ratio of Carbon:Hydrogen Lost to the Catalyst During the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Chromia/K/alumina Catalyst at 550°C.
(Catalyst weight = 0.2164 g).

Pulse	1 (C_3D_8)	2 (C_3H_8)	3 (C_3D_8)	4 (C_3H_8)	5 (C_3D_8)	6 (C_3H_8)	Total
Ratio of C:H Lost to Catalyst	1:6	1:4	1:7	1:5	1:9	1:5	1:5

Figure 5.7c Hydrogen Balance for the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Chromia/K/alumina Catalyst at 550°C. (Catalyst weight = 0.2164 g).

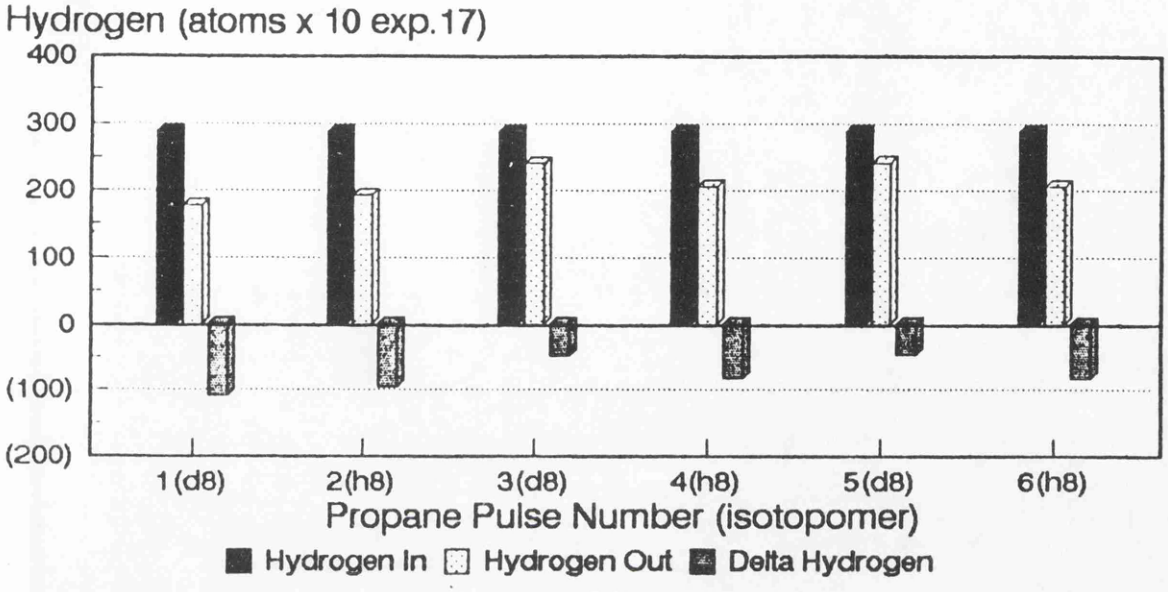


Table 5.10e Oxygen Balance for the Interaction of Dioxygen with the Used Chromia/K/alumina Catalyst at 550°C.
(Catalyst weight = 0.2164 g).

Molecules x 10^{17}

Pulse	O_2 In	O_2 Out	CO Out	CO_2 Out	O_2 Taken Up
1(O_2)	36.0	0.0	0.5	0.5	35.2
2(O_2)	36.0	0.0	0.4	0.2	35.4
3(O_2)	36.0	0.5	0.0	0.1	35.4
4(O_2)	36.0	0.6	0.0	0.0	35.4
5(O_2)	36.0	1.0	0.0	trace	35.0
6(O_2)	36.0	2.4	0.0	trace	33.6
7(O_2)	36.0	4.0	0.0	0.0	32.0
8(O_2)	36.0	5.9	0.0	0.0	30.1

Total carbon burnt off catalyst as CO or CO_2 = 1.7 x 10^{17} atoms.

Table 5.10f Normalised Mass Spectra for Propene Produced During the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Chromia/K/alumina Catalyst at 550°C.

m/z	Pulse 1 C_3D_8*	Pulse 2 C_3H_8	Pulse 3 C_3D_8*	Pulse 4 C_3H_8	Pulse 5 C_3D_8*	Pulse 6 C_3H_8
36	0.00	0.08	0.00	0.10	0.20	0.09
37	0.33	0.21	0.00	0.24	0.00	0.23
38	1.00	0.25	0.50	0.10	0.80	0.36
39	1.33	1.04	1.25	0.86	1.20	1.05
40	1.33	0.42	3.50	0.62	1.60	0.36
41	2.00	1.00	1.50	1.00	1.00	1.00
42	3.27	0.75	2.65	0.81	2.00	0.73
43	2.00	0.79	2.00	0.95	1.60	0.95
44	0.00	0.33	0.00	0.38	0.00	0.36
45	0.00	0.00	0.25	0.10	0.60	0.09
46	1.00	0.00	1.00	0.00	1.00	0.00
47	0.00	0.00	0.00	0.05	0.00	0.05
48	0.77	0.04	0.78	0.05	0.20	0.00
49	0.00	0.04	0.75	0.00	0.40	0.05
50	0.04	0.04	0.42	0.00	0.20	0.00
51	0.00	0.00	0.50	0.00	0.40	0.00
52	0.00	0.00	0.00	0.00	0.00	0.00

* The fragmentation pattern of perdeutero propane has also been subtracted because the perdeutero propane peak overlapped the perdeutero propene peak.

Table 5.10g Normalised Mass Spectra for Unreacted Propane During the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Chromia/K/alumina Catalyst at 550°C.

m/z	Pulse 1 C_3D_8	Pulse 2 C_3H_8	Pulse 3 C_3D_8	Pulse 4 C_3H_8	Pulse 5 C_3D_8	Pulse 6 C_3H_8
36	0.00	0.10	0.00	0.00	0.17	0.08
37	0.17	0.34	0.00	0.23	0.50	0.25
38	1.83	0.54	0.86	0.00	1.67	0.08
39	2.33	1.59	2.86	0.89	1.83	0.86
40	3.33	0.78	8.00	0.81	2.50	0.41
41	3.00	1.51	4.00	1.26	1.75	1.14
42	6.00	1.30	5.63	1.19	3.03	0.97
43	3.00	1.00	3.14	1.00	2.83	1.00
44	0.00	0.00	0.00	0.00	0.00	0.00
45	0.00	0.00	0.00	0.09	1.00	0.08
46	0.25	0.00	0.14	0.02	0.00	0.05
47	0.00	0.00	0.00	0.08	0.00	0.05
48	1.01	0.10	2.74	0.10	0.41	0.00
49	0.00	0.00	0.00	0.02	0.50	0.02
50	0.00	0.00	0.43	0.04	0.00	0.00
51	1.00	0.00	1.00	0.04	0.00	0.00
52	0.00	0.00	0.00	0.04	0.00	0.00

Experiment C(K)ADPR.13

Table 5.11a Product Distribution for the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Chromia/K/alumina Catalyst at 600°C. (Catalyst weight = 0.2183 g; pulse size = 36.0 x 10^{17} molecules).

Product molecules x 10^{17}

Pulse	CO	CX_4	CO_2	C_2X_6	C_3X_6	C_3X_8
1(C_3D_8)	8.1	0.0	0.6	0.8	11.4	15.4
2(C_3H_8)	4.7	0.4	0.5	0.9	16.5	10.6
3(C_3D_8)	4.7	0.3	0.8	0.8	12.5	18.0
4(C_3H_8)	10.1	0.0	1.3	1.0	15.9	10.4
5(C_3D_8)	4.6	0.2	1.2	0.9	11.6	17.1
6(C_3H_8)	6.7	0.3	1.2	0.9	15.7	10.6

Table 5.11b Carbon Balance for the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Chromia/K/alumina Catalyst at 600°C. (Catalyst weight = 0.2183 g).

Carbon atoms x 10^{17}

Pulse	Carbon In	Carbon Out	Delta Carbon
1(C_3D_8)	108.0	90.7	-17.3
2(C_3H_8)	108.0	88.7	-19.3
3(C_3D_8)	108.0	98.9	-9.1
4(C_3H_8)	108.0	92.3	-15.7
5(C_3D_8)	108.0	93.9	-14.1
6(C_3H_8)	108.0	88.9	-19.1

Total carbon lost to the catalyst = 94.6 x 10^{17} atoms.

Experiment C(K)ADPR.13

Figure 5.8a Product Distribution for the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Chromia/K/alumina Catalyst at 600°C. (Catalyst weight = 0.2183 g; pulse size = 36.0 x 10^{17} molecules).

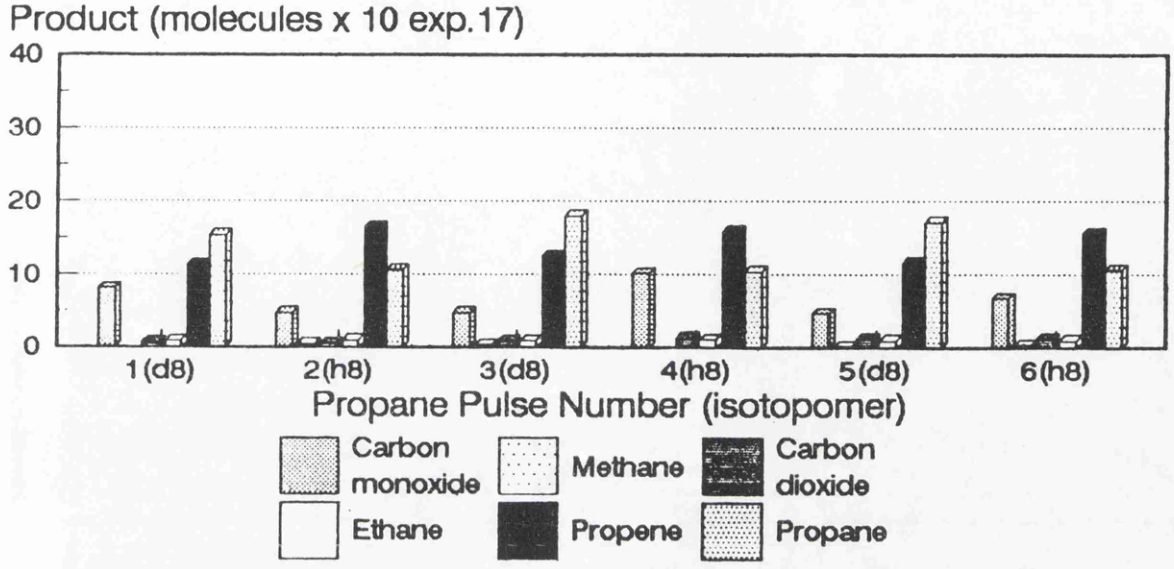


Figure 5.8b Carbon Balance for the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Chromia/K/alumina Catalyst at 600°C. (Catalyst weight = 0.2183 g).

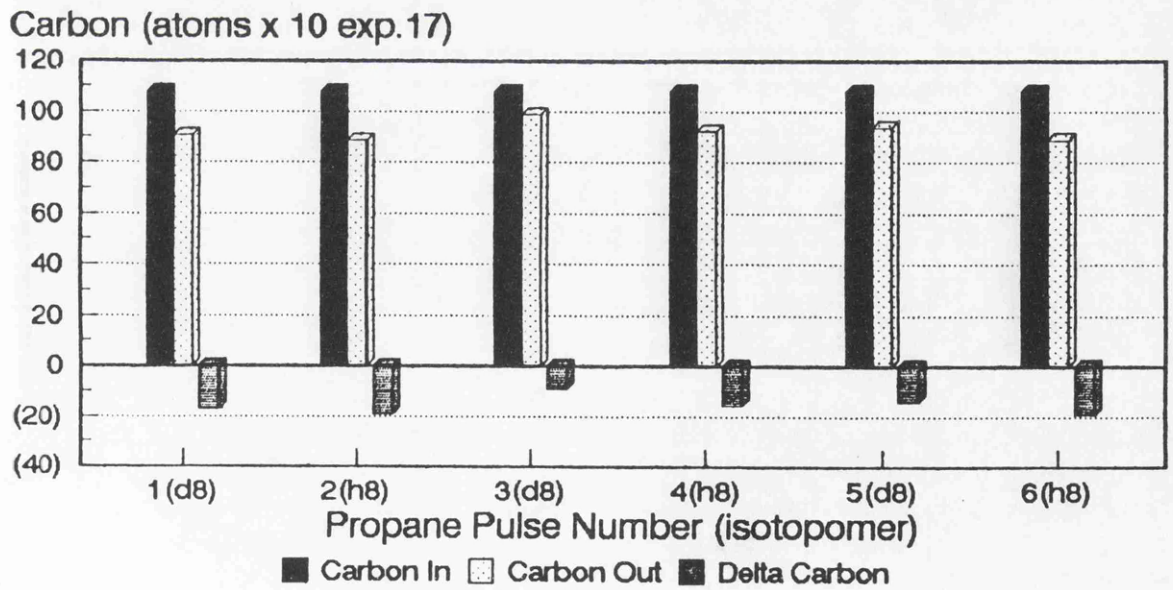


Table 5.11c Hydrogen Balance for the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Chromia/K/alumina Catalyst at 600°C. (Catalyst weight = 0.2183 g).

Hydrogen atoms x 10^{17}

Pulse	Hydrogen In	Hydrogen Out	Delta Hydrogen
1(C_3D_8)	288.0	196.4	-91.6
2(C_3H_8)	288.0	190.8	-97.2
3(C_3D_8)	288.0	225.0	-63.0
4(C_3H_8)	288.0	184.6	-103.4
5(C_3D_8)	288.0	212.6	-75.4
6(C_3H_8)	288.0	185.6	-102.4

Total hydrogen lost to the catalyst = 533.0 x 10^{17} atoms.

Table 5.11d Ratio of Carbon:Hydrogen Lost to the Catalyst During the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Chromia/K/alumina Catalyst at 600°C.
(Catalyst weight = 0.2183 g).

Pulse	1 (C_3D_8)	2 (C_3H_8)	3 (C_3D_8)	4 (C_3H_8)	5 (C_3D_8)	6 (C_3H_8)	Total
Ratio of C:H Lost to Catalyst	1:5	1:5	1:7	1:6	1:5	1:5	1:6

Figure 5.8c Hydrogen Balance for the Interaction of Alternate Pulses of C_3D_8 and C_3H_8 with a Chromia/K/alumina Catalyst at 600°C. (Catalyst weight = 0.2183 g).

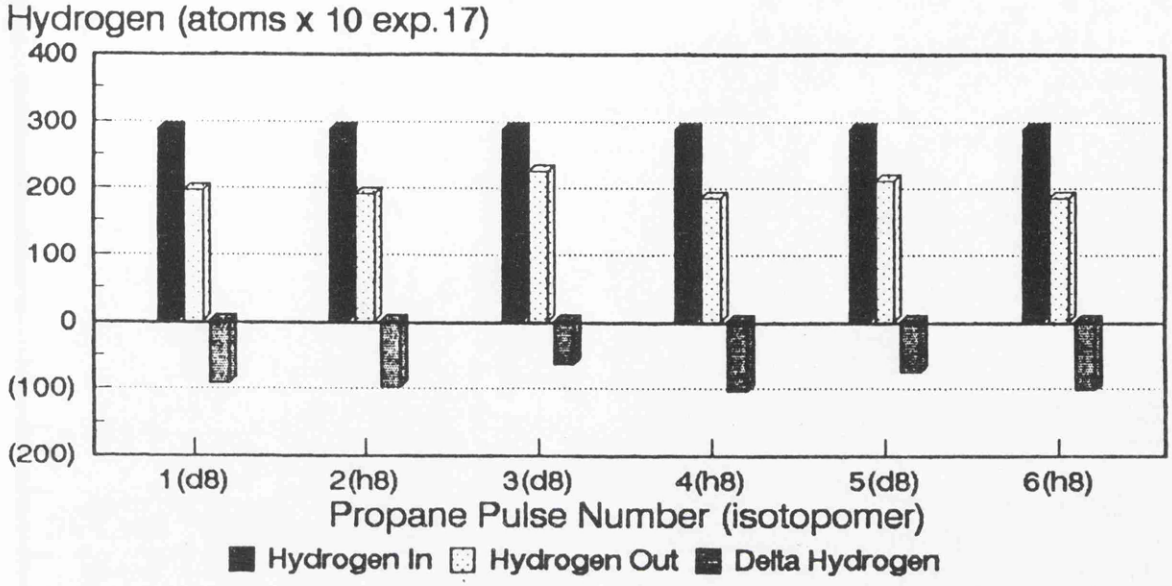


Table 5.11e Oxygen Balance for the Interaction of Dioxygen with the Used Chromia/K/alumina Catalyst at 600°C.
(Catalyst weight = 0.2183 g).

Molecules x 10^{17}

Pulse	O_2 In	O_2 Out	CO Out	CO_2 Out	O_2 Taken Up
1(O_2)	36.0	0.0	0.4	0.6	35.2
2(O_2)	36.0	0.0	0.4	0.3	35.5
3(O_2)	36.0	0.0	0.3	0.3	35.6
4(O_2)	36.0	0.8	0.0	0.4	34.8
5(O_2)	36.0	1.7	0.0	0.4	33.9
6(O_2)	36.0	3.8	0.0	0.3	31.9
7(O_2)	36.0	7.3	0.0	0.3	28.4
8(O_2)	36.0	11.9	0.0	0.2	23.9
9(O_2)	36.0	12.1	0.0	0.1	23.8
10(O_2)	36.0	18.4	0.0	0.0	17.6

Total carbon burnt off catalyst as CO or CO_2 = 3.9 x 10^{17} atoms.

Experiment C(K)ACPR.01

Table 5.12a Product Distribution for the Interaction of Pulses of (2-^{13}C)-C_3H_8 and C_3H_8 with a Chromia/K/alumina Catalyst at 500°C. (Catalyst weight = 0.2148 g; pulse size 36.0 x 10^{17} molecules).

Product molecules x 10^{17}

Pulse	CO	CX_4	CO_2	C_2X_6	C_3X_6	C_3X_8
1	1.6	0.3	3.3	0.0	10.4	20.2
2	0.5	0.0	0.8	0.0	11.8	23.5
3 (2-^{13}C)	3.7	0.0	1.1	trace	10.4	20.6
4 (2-^{13}C)	6.5	0.0	1.6	0.0	7.3	18.7
5 (2-^{13}C)	5.1	0.0	1.0	0.2	7.7	19.8
6	1.0	0.3	0.9	0.0	10.1	23.1
7	1.4	0.3	0.8	0.2	9.9	23.2

Table 5.12b Carbon Balance for the Interaction of Pulses of (2-^{13}C)-C_3H_8 and C_3H_8 with a Chromia/K/alumina Catalyst at 500°C. (Catalyst weight 0.2148 g).

Carbon atoms x 10^{17}

Pulse	Carbon In	Carbon Out	Delta Carbon
1	108.0	97.0	-11.0
2	108.0	107.2	-0.8
3 (2-^{13}C)	108.0	97.8	-10.2
4 (2-^{13}C)	108.0	86.1	-21.9
5 (2-^{13}C)	108.0	89.0	-19.0
6	108.0	101.8	-6.2
7	108.0	102.2	-5.8

Total carbon lost to the catalyst = 74.9 x 10^{17} atoms.

Experiment C(K)ACPR.01

Figure 5.9a Product Distribution for the Interaction of Pulses of (2-^{13}C)-C_3H_8 and C_3H_8 with a Chromia/K/alumina Catalyst at 500°C. (Catalyst weight = 0.2148 g; pulse size 36.0 x 10^{17} molecules).

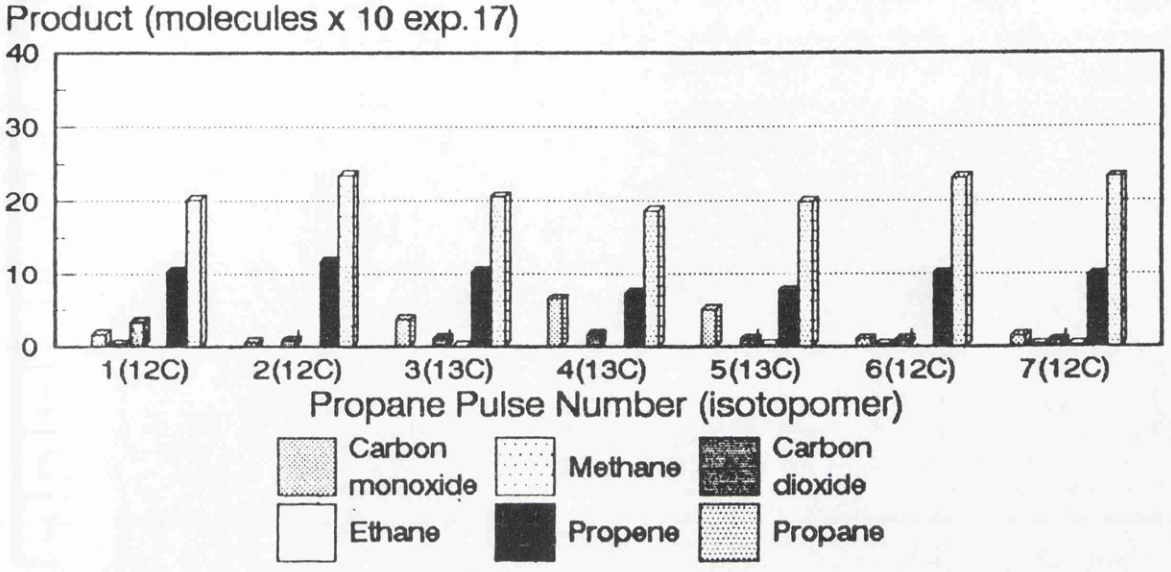


Figure 5.9b Carbon Balance for the Interaction of Pulses of (2-^{13}C)-C_3H_8 and C_3H_8 with a Chromia/K/alumina Catalyst at 500°C. (Catalyst weight 0.2148 g).

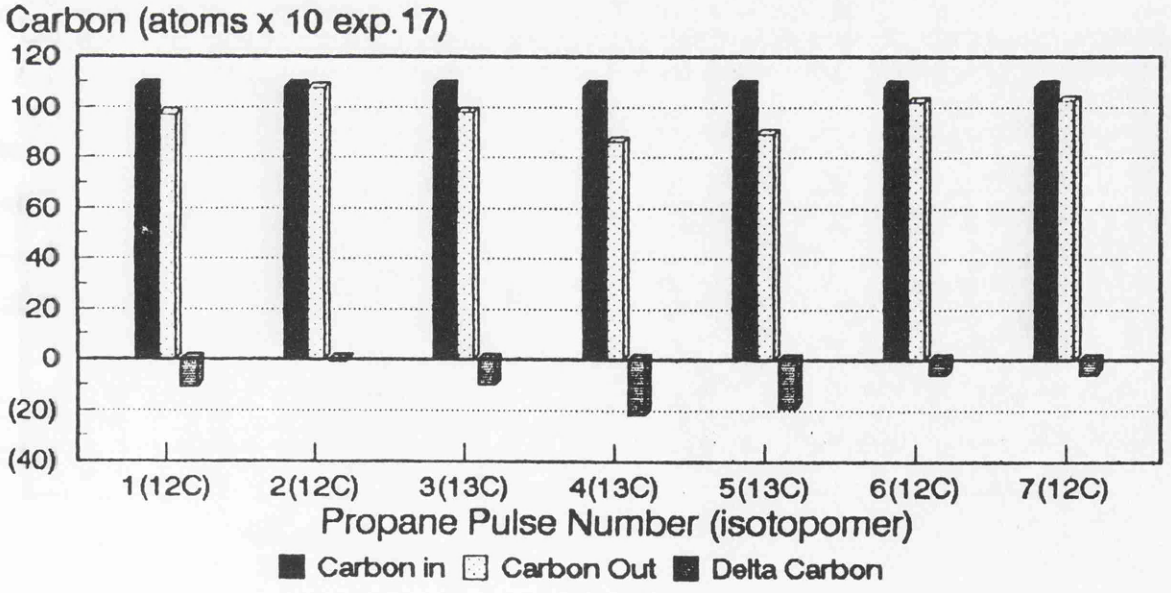


Table 5.12c Hydrogen Balance for the Interaction of Pulses of (2-^{13}C)-C_3H_8 and C_3H_8 with a Chromia/K/alumina Catalyst at 500°C. (Catalyst weight = 0.2148 g).

Hydrogen atoms x 10^{17}

Pulse	Hydrogen In	Hydrogen Out	Delta Hydrogen
1	288.0	225.2	-62.8
2	288.0	258.8	-29.2
3 (2-^{13}C)	288.0	227.2	-60.8
4 (2-^{13}C)	288.0	193.4	-94.6
5 (2-^{13}C)	288.0	205.8	-82.2
6	288.0	246.6	-41.4
7	288.0	247.4	-40.6

Total hydrogen lost to the catalyst = 411.6 x 10^{17} atoms.

Table 5.12d Ratio of Carbon:Hydrogen Lost to the Catalyst During the Interaction of Pulses of (2-^{13}C)-C_3H_8 and C_3H_8 with a Chromia/K/alumina Catalyst at 500°C.
(Catalyst weight = 0.2148 g).

Pulse	1	2	3 (^{13}C)	4 (^{13}C)	5 (^{13}C)	6	7	Total
Ratio of C:H Lost to Catalyst	1:6	1:29	1:6	1:4	1:4	1:7	1:7	1:6

Figure 5.9c Hydrogen Balance for the Interaction of Pulses of (2-^{13}C)-C_3H_8 and C_3H_8 with a Chromia/K/alumina Catalyst at 500°C. (Catalyst weight = 0.2148 g).

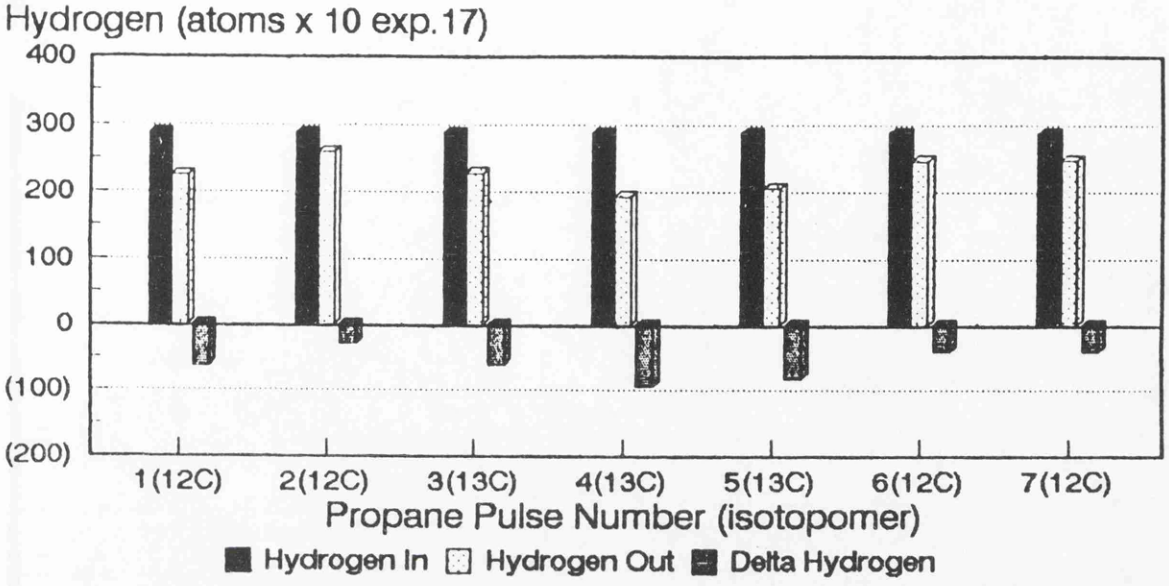


Table 5.12e Oxygen Balance for the Interaction of Dioxygen with the Used Chromia/K/alumina Catalyst at 500°C.
(Catalyst weight = 0.2148 g).

Molecules x 10^{17}

Pulse	O_2 In	O_2 Out	CO Out	CO_2 Out	O_2 Taken Up
1(O_2)	36.0	0.0	0.5	2.6	33.2
2(O_2)	36.0	0.0	0.5	1.2	34.6
3(O_2)	36.0	0.5	0.0	0.9	34.6
4(O_2)	36.0	0.6	0.0	0.7	34.8
5(O_2)	36.0	1.1	0.0	0.6	34.3
6(O_2)	36.0	2.1	0.0	0.5	33.4
7(O_2)	36.0	4.7	0.0	0.4	30.9
8(O_2)	36.0	7.4	0.0	0.3	28.3
9(O_2)	36.0	11.5	0.0	0.2	24.3
10(O_2)	36.0	16.6	0.0	0.1	19.3
11(O_2)	36.0	17.5	0.0	0.0	18.5
12(O_2)	36.0	24.2	0.0	0.0	11.8

Total carbon burnt off catalyst as CO or CO_2 = 8.5 x 10^{17} atoms.

Table 5.12f Ratio of $^{12}CH_4$:$^{13}CH_4$ Produced During the Interaction of Pulses of C_3H_8 and (2-^{13}C)-C_3H_8 with a Chromia/K/alumina Catalyst at 500°C.

Pulse	1	2	3 (^{13}C)	4 (^{13}C)	5 (^{13}C)	6	7
$^{12}CH_4$:$^{13}CH_4$	38:1	51:1	6:1	8:1	9:1	36:1	29:1

Table 5.12g Normalised Mass Spectra for Propene Produced During the Interaction of Pulses of C_3H_8 and (2-^{13}C)-C_3H_8 with a Chromia/K/alumina Catalyst at 500°C.

m/z	Pulse 1	Pulse 2	Pulse 3 (2-^{13}C)	Pulse 4 (2-^{13}C)	Pulse 5 (2-^{13}C)	Pulse 6	Pulse 7
36	0.04	0.03	0.00	0.00	0.04	0.04	0.03
37	0.16	0.18	0.04	0.04	0.04	0.17	0.17
38	0.23	0.24	0.19	0.19	0.19	0.24	0.23
39	0.87	0.89	0.33	0.33	0.33	0.88	0.88
40	0.25	0.26	0.95	0.94	0.92	0.26	0.27
41	1.00	1.00	0.29	0.29	0.29	1.00	1.00
42	0.60	0.58	1.00	1.00	1.00	0.60	0.61
43	0.20	0.24	0.53	0.55	0.54	0.16	0.11
44	0.18	0.18	0.55	0.56	0.55	0.08	0.09
45	0.00	0.00	0.37	0.39	0.39	0.01	0.01
46	0.00	0.00	0.00	0.03	0.01	0.00	0.00

Table 5.12h Normalised Mass Spectra of Unreacted Propane During the Interaction of Pulses of C_3H_8 and (2-^{13}C)-C_3H_8 with a Chromia/K/alumina Catalyst at 500°C.

m/z	Pulse 1	Pulse 2	Pulse 3 (2-^{13}C)	Pulse 4 (2-^{13}C)	Pulse 5 (2-^{13}C)	Pulse 6	Pulse 7
36	0.05	0.05	0.00	0.00	0.00	0.06	0.05
37	0.28	0.33	0.09	0.07	0.08	0.33	0.28
38	0.43	0.49	0.38	0.39	0.40	0.51	0.44
39	1.34	1.49	0.67	0.68	0.67	1.57	1.38
40	0.14	0.21	1.03	1.66	1.65	0.23	0.21
41	0.97	1.08	0.18	0.33	0.30	1.15	1.01
42	0.32	0.36	0.74	1.27	1.23	0.38	0.33
43	1.41	1.52	0.51	0.57	0.52	1.65	1.49
44	1.00	1.00	1.63	1.63	1.63	1.00	1.00
45	0.02	0.03	1.00	1.00	1.00	0.04	0.03
46	0.00	0.00	0.00	0.05	0.02	0.00	0.00

Table 5.12i Ratio of $^{12}CO_2$:$^{13}CO_2$ Produced During the Interaction of Pulses of Dioxygen with a Used Chromia/K/alumina Catalyst at 500°C.

Pulse	1	2	3	4	5	6
$^{12}CO_2$: $^{13}CO_2$	5:1	7:1	8:1	7:1	7:1	7:1
Pulse	7	8	9	10	11	12
$^{12}CO_2$: $^{13}CO_2$	6:1	7:1	7:1	8:1	18:1	45:1

Experiment C(K)ACPR.02

Table 5.13a Product Distribution for the Interaction of Pulses of (2-^{13}C)-C_3H_8 and C_3H_8 with a Chromia/K/alumina Catalyst at 550°C. (Catalyst weight = 0.2198 g; pulse size = 36.0 x 10^{17}).

Product molecules x 10^{17}

Pulse	CO	CX_4	CO_2	C_2X_6	C_3X_6	C_3X_8
1	3.2	0.5	3.2	0.6	12.5	16.0
2	13.3	0.0	1.9	0.2	9.5	11.5
3 (2-^{13}C)	20.2	0.0	2.9	0.2	5.9	7.6
4 (2-^{13}C)*	12.7	0.0	2.3	0.1	7.0	9.5
5	2.0	0.5	1.1	0.1	14.5	17.5
6	3.0	0.4	1.3	0.3	14.2	17.6

* Pulse size = 31.7 x 10^{17}.

Table 5.13b Carbon Balance for the Interaction of Pulses of (2-^{13}C)C_3H_8 and C_3H_8 with a Chromia/K/alumina Catalyst at 550°C. (Catalyst weight = 0.2198 g).

Carbon atoms x 10^{17}

Pulse	Carbon In	Carbon Out	Delta Carbon
1	108.0	93.6	-14.4
2	108.0	78.6	-29.4
3 (2-^{13}C)	108.0	64.0	-44.0
4 (2-^{13}C)	95.0	64.7	-30.3
5	108.0	99.8	-8.2
6	108.0	100.7	-7.3

Total carbon lost to the catalyst = 133.6 x 10^{17} atoms.

Experiment C(K)ACPR.02

Figure 5.10a Product Distribution for the Interaction of Pulses of (2-^{13}C)-C_3H_8 and C_3H_8 with a Chromia/K/alumina Catalyst at 550°C. (Catalyst weight = 0.2198 g; pulse size = 36.0 x 10^{17}).

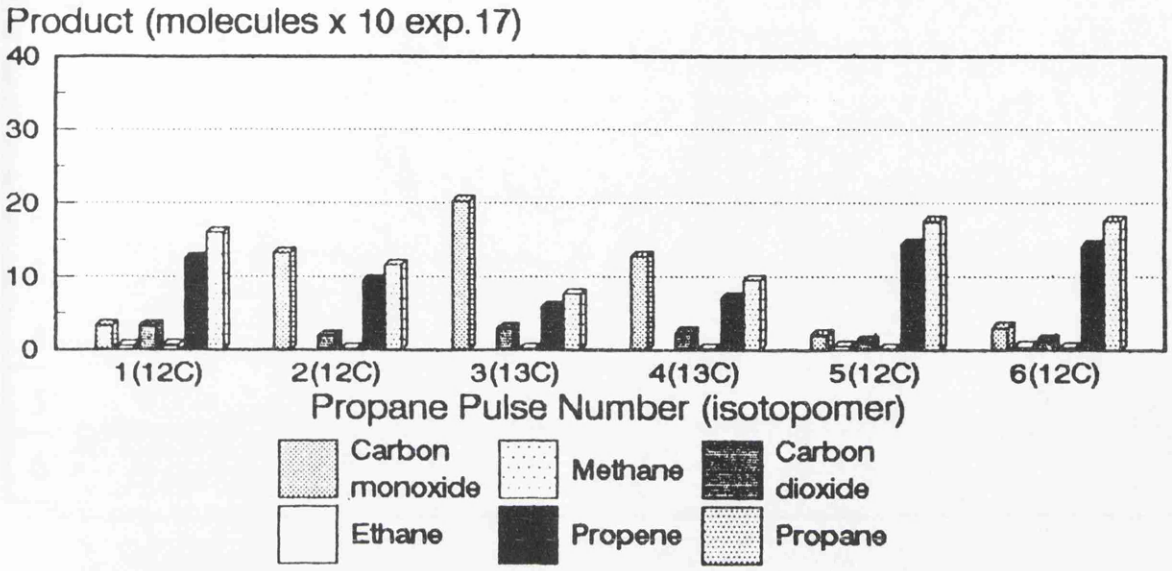


Figure 5.10b Carbon Balance for the Interaction of Pulses of (2-^{13}C)C_3H_8 and C_3H_8 with a Chromia/K/alumina Catalyst at 550°C. (Catalyst weight = 0.2198 g).

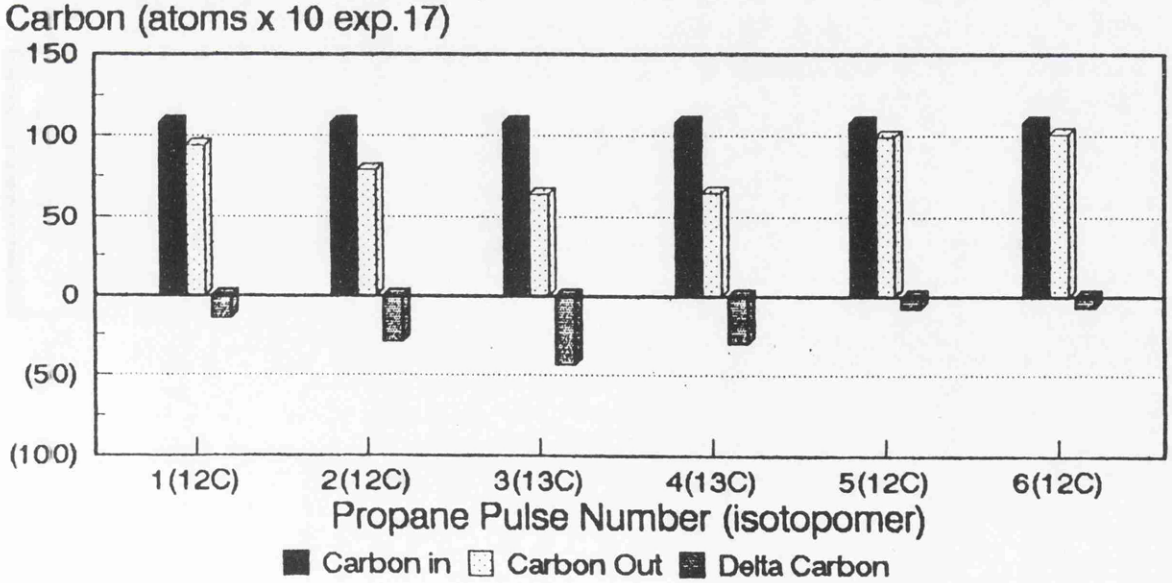


Table 5.13c Hydrogen Balance for the Interaction of Pulses of (2-^{13}C)-C_3H_8 and C_3H_8 with a Chromia/K/alumina Catalyst at 550°C. (Catalyst weight = 0.2198 g).

Hydrogen atoms x 10^{17}

Pulse	Hydrogen In	Hydrogen Out	Delta Hydrogen
1	288.0	208.6	-79.4
2	288.0	150.2	-137.8
3 (2-^{13}C)	288.0	97.4	-190.6
4 (2-^{13}C)	253.0	118.6	-134.4
5	288.0	229.6	-58.4
6	288.0	229.4	-58.6

Total hydrogen lost to the catalyst = 659.2 x 10^{17} atoms.

Table 5.13d Ratio of Carbon:Hydrogen Lost to the Catalyst During the Interaction of Pulses of (2-^{13}C)-C_3H_8 and C_3H_8 with a Chromia/K/alumina Catalyst at 550°C.
(Catalyst weight = 0.2198 g).

Pulse	1	2	3 (2-^{13}C)	4 (2-^{13}C)	5	6	Total
Ratio of C:H Lost to Catalyst	1:6	1:5	1:4	1:4	1:7	1:8	1:5

Figure 5.10c Hydrogen Balance for the Interaction of Pulses of (2-^{13}C)-C_3H_8 and C_3H_8 with a Chromia/K/alumina Catalyst at 550°C. (Catalyst weight = 0.2198 g).

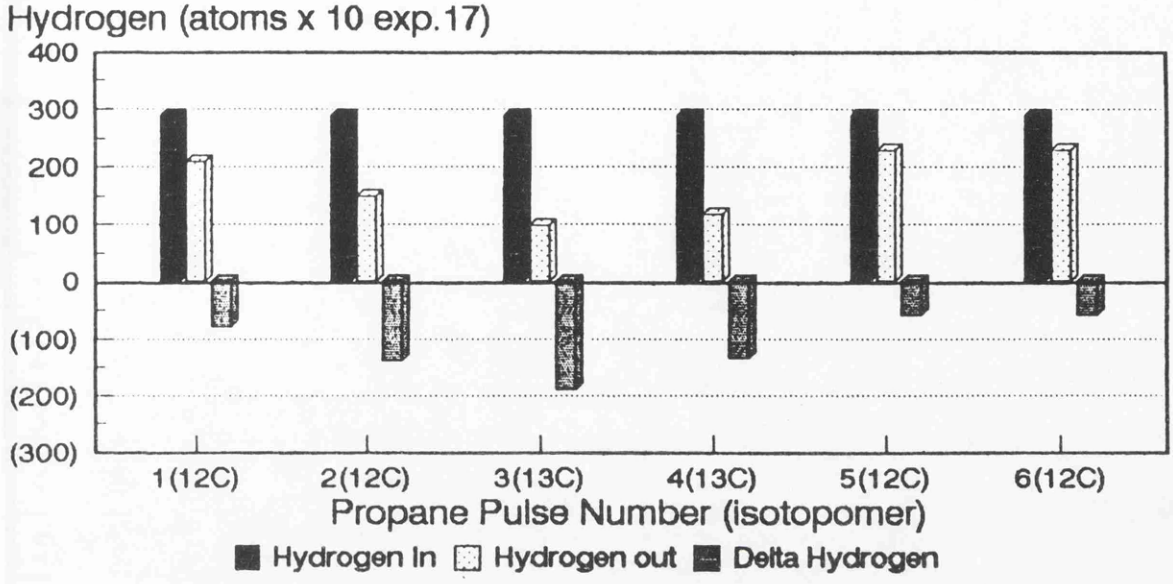


Table 5.13e Oxygen Balance for the Interaction of Dioxygen with the Used Chromia/K/alumina Catalyst at 550°C.
(Catalyst weight = 0.2198 g).

Molecules x 10^{17}

Pulse	O_2 In	O_2 Out	CO Out	CO_2 Out	O_2 Taken Up
1(O_2)	36.0	0.3	0.0	0.6	35.1
2(O_2)	36.0	0.4	0.0	0.3	35.3
3(O_2)	36.0	0.6	0.0	0.3	35.1
4(O_2)	36.0	0.4	0.0	0.2	32.5
5(O_2)	36.0	0.4	0.0	0.2	35.4
6(O_2)	36.0	0.4	0.0	0.3	35.3

Total carbon burnt off catalyst as CO or CO_2 = 1.9 x 10^{17} atoms.

Table 5.13f Ratio of $^{12}CH_4$:$^{13}CH_4$ Produced from the Interaction of Pulses of C_3H_8 and (2-^{13}C)-C_3H_8 with a Chromia/K/alumina Catalyst at 550°C.

Pulse	1	2	3 (^{13}C)	4 (^{13}C)	5	6
$^{12}CH_4$:$^{13}CH_4$	∞[a]	∞[a]	2:1	3:1	15:1	24:1

[a] ∞ means only $^{12}CH_4$ was observed.

Table 5.13g Normalised Mass Spectra for Propene Produced During the Interaction of Pulses of C_3H_8 and (2-^{13}C)-C_3H_8 with a Chromia/K/alumina Catalyst at 550°C.

m/z	Pulse 1	Pulse 2	Pulse 3 (2-^{13}C)	Pulse 4 (2-^{13}C)	Pulse 5	Pulse 6
36	0.00	0.03	0.00	0.00	0.03	0.03
37	0.19	0.15	0.05	0.09	0.18	0.18
38	0.96	0.22	0.17	0.20	0.26	0.25
39	1.12	0.83	0.31	0.35	0.94	0.95
40	0.28	0.33	0.82	0.94	0.27	0.27
41	1.00	1.00	0.34	0.31	1.00	1.00
42	0.54	0.62	1.00	1.00	0.55	0.54
43	0.48	0.03	0.56	0.52	0.38	0.48
44	0.44	0.03	0.03	0.52	0.24	0.30
45	0.00	0.00	0.01	0.04	0.02	0.01
46	0.00	0.00	0.00	0.02	0.01	0.01

Table 5.13h Normalised Mass Spectra of Unreacted Propane During the Interaction of Pulses of C_3H_8 and (2-^{13}C)-C_3H_8 with a Chromia/K/alumina Catalyst at 550°C.

m/z	Pulse 1	Pulse 2	Pulse 3 (2-^{13}C)	Pulse 4 (2-^{13}C)	Pulse 5	Pulse 6
36	0.00	0.02	0.00	0.00	0.04	0.03
37	0.25	0.09	0.08	0.07	0.27	0.25
38	0.40	0.15	0.32	0.30	0.42	0.39
39	1.25	0.48	0.61	0.52	1.34	1.29
40	0.27	0.12	1.37	1.33	0.22	0.20
41	0.95	0.37	0.29	0.26	1.04	1.01
42	0.32	0.12	1.05	1.03	0.36	0.34
43	1.37	0.53	0.48	0.43	1.54	1.53
44	1.00	1.00	1.53	1.77	1.00	1.00
45	0.03	0.01	1.00	1.00	0.04	0.03
46	0.00	0.00	0.04	0.03	0.00	0.01

Table 5.13i Ratio of $^{12}CO_2$:$^{13}CO_2$ Produced During the Interaction of Pulses of Dioxygen with a Used Chromia/K/alumina Catalyst at 550°C.

Pulse	1	2	3	4	5	6
$^{12}CO_2$: $^{13}CO_2$	42:1	21:1	22:1	13:1	24:1	165:1

5.3 HYDROGENATION

Experiments were carried out to determine the activity of the catalysts towards hydrogenation. This was done by passing propyne over a reduced catalyst charge using the gas adsorption apparatus, described in Section 3.3, following the reaction procedure outlined in Section 3.4.

All hydrogenation experiments involved the use of unlabelled propyne. In order to follow the hydrogen during the hydrogenation reaction, an experiment was carried out using a chromia/K/alumina catalyst reduced in deterium instead of in 6% hydrogen/nitrogen, Experiment C(K)ADPRY.01.

The results of these experiments are given in Tables 5.14a - 5.20e and Figures 5.11a - 5.17c.

Note

Experimental codes used in this section are as follows:-

1. The first two, or three, letters of the code refers to the catalyst used:-

   PA = platinum/alumina

   C(K)A = chromia/alumina promoted with potassium.

2. When the catalyst was reduced in deuterium, as opposed to 6% hydrogen/nitrogen, this is indicated by a D after the catalyst code

letters.

3. The remaining group of letters refers to the gas used in the experiment:-

   PRY = propyne.

4. Finally, the two digits at the end of the code are the experiment number for a particular catalyst and experiment type as described by the letters of the code.

Hydrogenation Experiments

Experiment	Catalyst	Temperature	Gases
PAPRY.01	Pt/alumina	500°C	C_3H_4
PAPRY.02	Pt/alumina	550°C	C_3H_4
PAPRY.03	Pt/alumina	600°C	C_3H_4
C(K)APRY.01	Chromia/K/alumina	500°C	C_3H_4
C(K)APRY.02	Chromia/K/alumina	550°C	C_3H_4
C(K)APRY.03	Chromia/K/alumina	600°C	C_3H_4
C(K)ADPRY.01	Chromia/K/alumina (reduced in deuterium)	600°C	C_3H_4

Experiment PAPRY.01

Table 5.14a Product Distribution for the Interaction of Pulses of C_3H_4 with a Pt/alumina Catalyst at 500°C.
(Catalyst weight = 0.2151 g; Pulse size = 36.0 x 10^{17} molecules).

Product molecules x 10^{17}

Pulse	CO	CH_4	CO_2
1 (C_3H_4)	44.0	22.3	28.3
2 (C_3H_4)	49.8	30.2	6.9
3 (C_3H_4)	57.0	27.2	0.0
4 (C_3H_4)	53.1	38.8	0.0
5 (C_3H_4)	46.8	34.2	0.0
6 (C_3H_4)	46.3	27.5	0.0

Table 5.14b Carbon Balance for the Interaction of Pulses of C_3H_4 with a Pt/alumina Catalyst at 500°C.
(Catalyst weight = 0.2151 g).

Carbon atoms x 10^{17}

Pulse	Carbon In	Carbon Out	Delta Carbon
1 (C_3H_4)	108.0	94.6	-13.4
2 (C_3H_4)	108.0	86.9	-21.1
3 (C_3H_4)	108.0	84.2	-23.8
4 (C_3H_4)	108.0	91.9	-16.1
5 (C_3H_4)	108.0	81.0	-27.0
6 (C_3H_4)	108.0	73.8	-34.2

Total carbon lost to the catalyst = 135.6 x 10^{17} atoms.

Experiment PAPRY.01

Figure 5.11a Product Distribution for the Interaction of Pulses of C_3H_4 with a Pt/alumina Catalyst at 500°C.
(Catalyst weight = 0.2151 g; Pulse size = 36.0 x 10^{17} molecules).

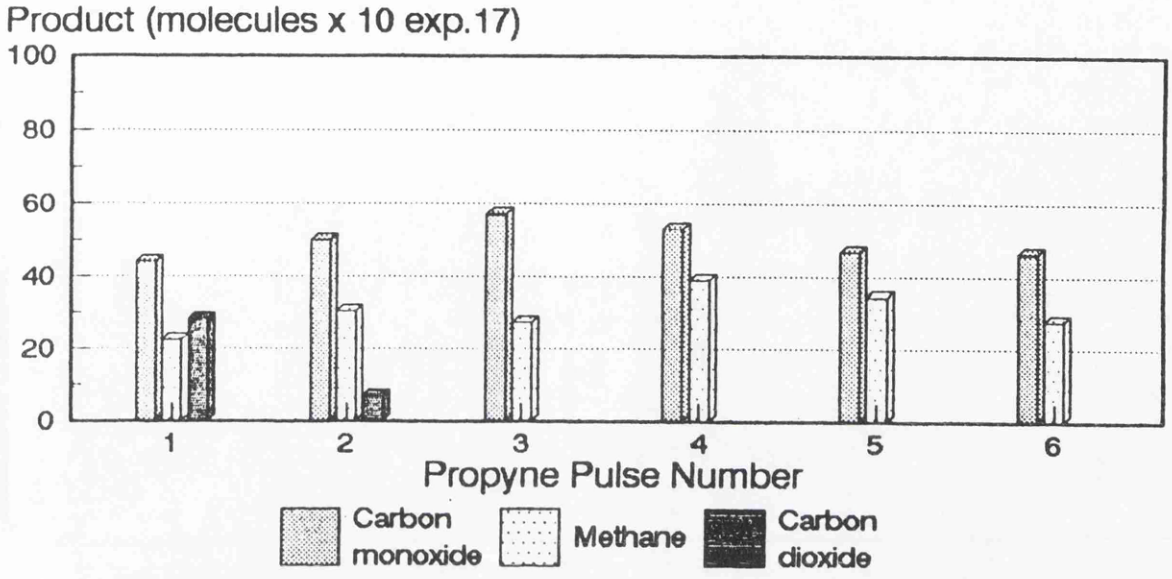


Figure 5.11b Carbon Balance for the Interaction of Pulses of C_3H_4 with a Pt/alumina Catalyst at 500°C.
(Catalyst weight = 0.2151 g).

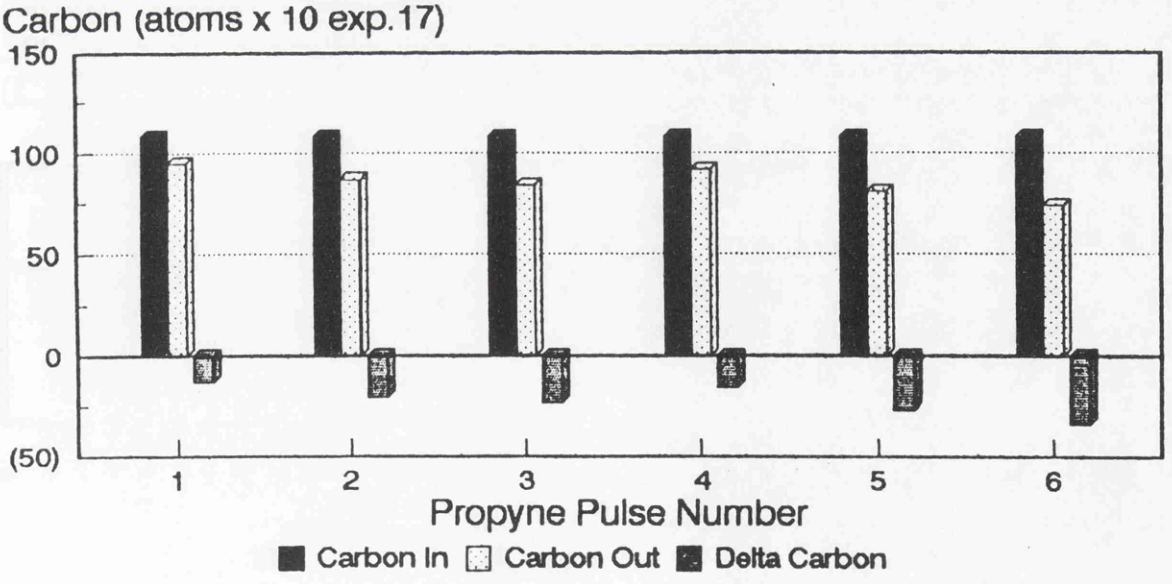


Table 5.14c Hydrogen Balance for the Interaction of Pulses of C_3H_4 with a Pt/alumina Catalyst at 500°C.
(Catalyst weight = 0.2151 g).

Hydrogen atoms x 10^{17}

Pulse	Hydrogen In	Hydrogen Out	Delta Hydrogen
1 (C_3H_4)	144.0	89.2	-54.8
2 (C_3H_4)	144.0	120.8	-23.2
3 (C_3H_4)	144.0	108.8	-35.2
4 (C_3H_4)	144.0	155.2	11.2
5 (C_3H_4)	144.0	136.8	-7.2
6 (C_3H_4)	144.0	110.0	-34.0

Total hydrogen lost to the catalyst = 143.2 x 10^{17} atoms.

Table 5.14d Ratio of Carbon:Hydrogen Lost to the Catalyst During the Interaction of Pulses of C_3H_4 with a Pt/alumina Catalyst at 500°C.
(Catalyst weight = 0.2151 g).

Pulse	1 (C_3H_4)	2 (C_3H_4)	3 (C_3H_4)	4 (C_3H_4)	5 (C_3H_4)	6 (C_3H_4)	Total
Ratio of C:H Lost to Catalyst	1:4	1:1	1:2	∞[a]	∞[a]	1:1	1:1

[a] ∞ means only carbon was lost to the catalyst.

Figure 5.11c Hydrogen Balance for the Interaction of Pulses of C_3H_4 with a Pt/alumina Catalyst at 500°C.
(Catalyst weight = 0.2151 g).

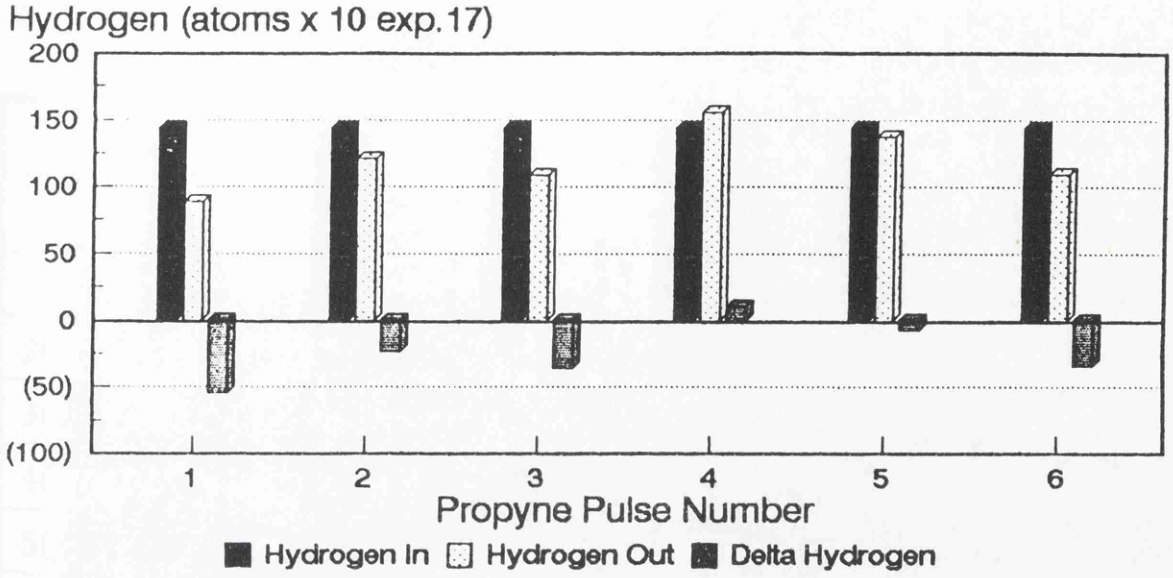


Table 5.14e Oxygen Balance for the Interaction of Dioxygen with the Used Pt/alumina Catalyst at 500°C.
(Catalyst weight = 0.2151 g)

Molecules x 10^{17}

Pulse	O_2 In	O_2 Out	CO Out	CO_2 Out	O_2 Taken Up
1(O_2)	36.0	0.0	3.8	29.9	4.2
2(O_2)	36.0	0.0	4.3	30.5	4.0
3(O_2)	36.0	0.0	3.4	27.9	6.4
4(O_2)	36.0	4.6	0.0	24.2	7.2
5(O_2)	36.0	25.2	0.0	2.7	8.1
6(O_2)	36.0	31.8	0.0	0.0	4.2
7(O_2)	36.0	31.0	0.0	0.0	5.0

Total carbon burnt off catalyst as CO or CO_2 = 126.7 x 10^{17} atoms.

Experiment PAPRY.02

Table 5.15a Product Distribution for the Interaction of Pulses of C_3H_4 with a Pt/alumina Catalyst at 550°C.
(Catalyst weight = 0.2018 g; Pulse size = 36.0 x 10^{17} molecules).

Product molecules x 10^{17}

Pulse	CO	CH_4	CO_2
1 (C_3H_4)	69.9	24.2	8.0
2 (C_3H_4)	65.2	21.0	3.1
3 (C_3H_4)	67.2	19.1	2.3
4 (C_3H_4)	51.0	27.7	0.0
5 (C_3H_4)	52.7	19.8	0.0
6 (C_3H_4)	48.9	19.3	0.0

Table 5.15b Carbon Balance for the Interaction of Pulses of C_3H_4 with a Pt/alumina Catalyst at 550°C.
(Catalyst weight = 0.2018 g).

Carbon atoms x 10^{17}

Pulse	Carbon In	Carbon Out	Delta Carbon
1 (C_3H_4)	108.0	102.1	-5.9
2 (C_3H_4)	108.0	89.3	-18.7
3 (C_3H_4)	108.0	88.6	-19.4
4 (C_3H_4)	108.0	78.7	-29.3
5 (C_3H_4)	108.0	72.5	-35.5
6 (C_3H_4)	108.0	68.2	-39.8

Total carbon lost to the catalyst = 148.6 x 10^{17} atoms.

Experiment PAPRY.02

Figure 5.12a Product Distribution for the Interaction of Pulses of C_3H_4 with a Pt/alumina Catalyst at 550°C.
(Catalyst weight = 0.2018 g; Pulse size = 36.0 x 10^{17} molecules).

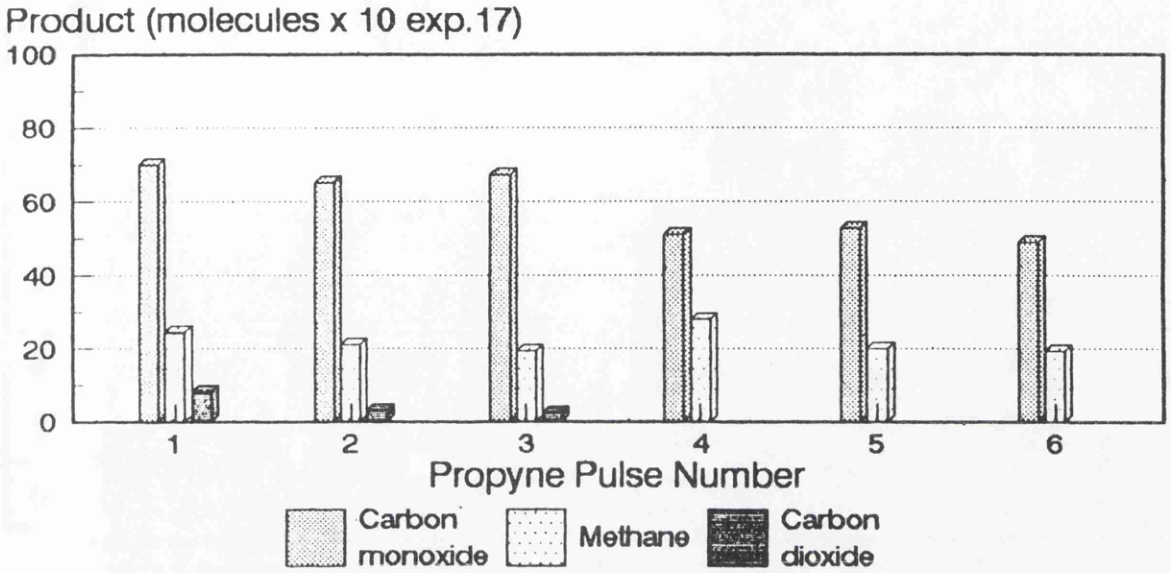


Figure 5.12b Carbon Balance for the Interaction of Pulses of C_3H_4 with a Pt/alumina Catalyst at 550°C.
(Catalyst weight = 0.2018 g).

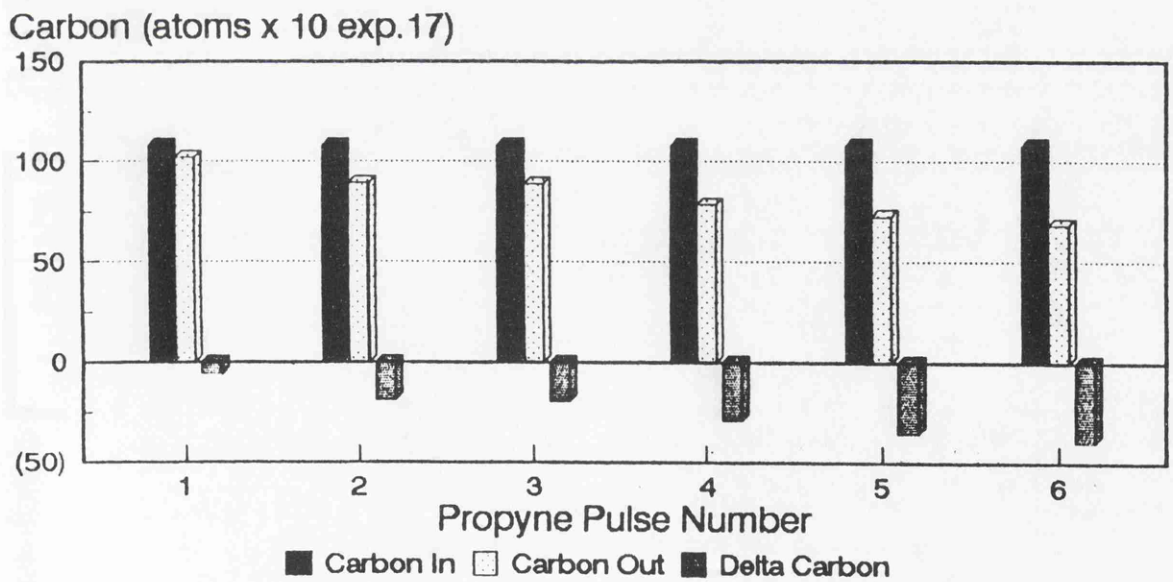


Table 5.15c Hydrogen Balance for the Interaction of Pulses of C_3H_4 with a Pt/alumina Catalyst at 550°C.
(Catalyst weight = 0.2018 g).

Hydrogen atoms x 10^{17}

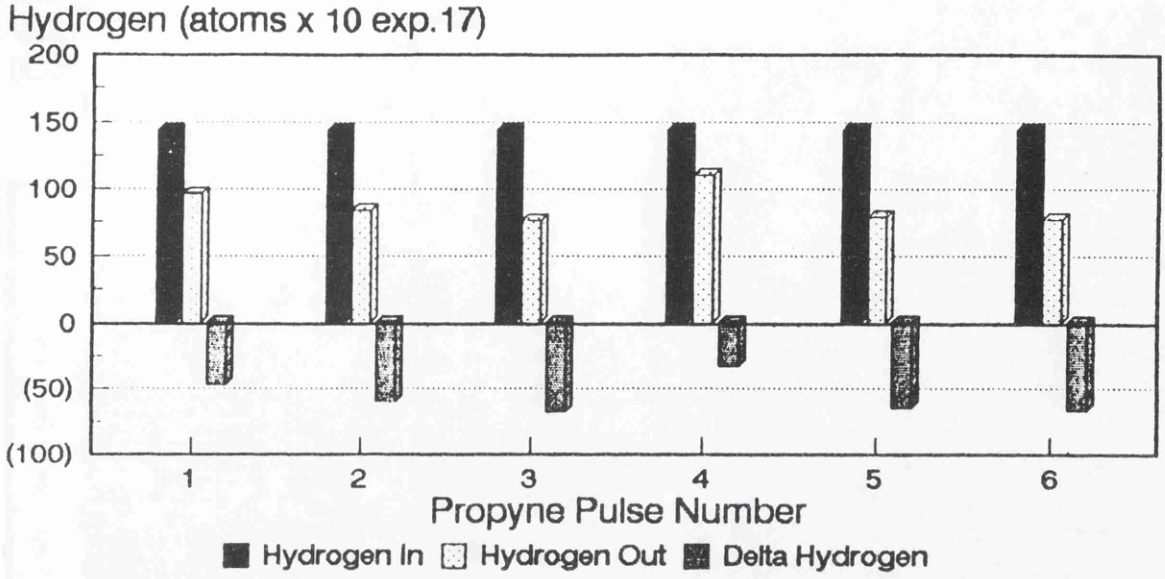
Pulse	Hydrogen In	Hydrogen Out	Delta Hydrogen
1 (C_3H_4)	144.0	96.8	-47.2
2 (C_3H_4)	144.0	84.0	-60.0
3 (C_3H_4)	144.0	76.4	-67.6
4 (C_3H_4)	144.0	110.8	-33.2
5 (C_3H_4)	144.0	79.2	-64.8
6 (C_3H_4)	144.0	77.2	-66.8

Total hydrogen lost to the catalyst = 339.6 x 10^{17} atoms.

Table 5.15d Ratio of Carbon:Hydrogen Lost to the Catalyst During the Interaction of Pulses of C_3H_4 with a Pt/alumina Catalyst at 500°C.
(Catalyst weight = 0.2018 g).

Pulse	1 (C_3H_4)	2 (C_3H_4)	3 (C_3H_4)	4 (C_3H_4)	5 (C_3H_4)	6 (C_3H_4)	Total
Ratio of C:H Lost to Catalyst	1:8	1:3	1:3	1:1	1:2	1:2	1:2

Figure 5.12c Hydrogen Balance for the Interaction of Pulses of C_3H_4 with a Pt/alumina Catalyst at 550°C.
(Catalyst weight = 0.2018 g).



Experiment PAPRY.03

Table 5.16a Product Distribution for the Interaction of Pulses of C_3H_4 with a Pt/alumina Catalyst at 600°C.
(Catalyst weight = 0.2242 g; Pulse size = 36.0 x 10^{17} molecules).

Product molecules x 10^{17}

Pulse	CO	CH_4	CO_2
1 (C_3H_4)	94.1	7.2	3.6
2 (C_3H_4)	79.9	9.8	1.6
3 (C_3H_4)	80.6	14.1	1.7
4 (C_3H_4)	62.1	9.8	4.6
5 (C_3H_4)	61.9	8.2	0.0
6 (C_3H_4)	51.1	8.0	0.0

Table 5.16b Carbon Balance for the Interaction of Pulses of C_3H_4 with a Pt/alumina Catalyst at 600°C.
(Catalyst weight = 0.2242 g).

Carbon atoms x 10^{17}

Pulse	Carbon In	Carbon Out	Delta Carbon
1 (C_3H_4)	108.0	104.9	-3.1
2 (C_3H_4)	108.0	91.3	-16.7
3 (C_3H_4)	108.0	96.4	-11.6
4 (C_3H_4)	108.0	76.5	-31.5
5 (C_3H_4)	108.0	70.1	-37.9
6 (C_3H_4)	108.0	59.1	-48.9

Total carbon lost to the catalyst = 149.7 x 10^{17} atoms.

Experiment PAPRY.03

Figure 5.13a Product Distribution for the Interaction of Pulses of C_3H_4 with a Pt/alumina Catalyst at 600°C.
(Catalyst weight = 0.2242 g; Pulse size = 36.0 x 10^{17} molecules).

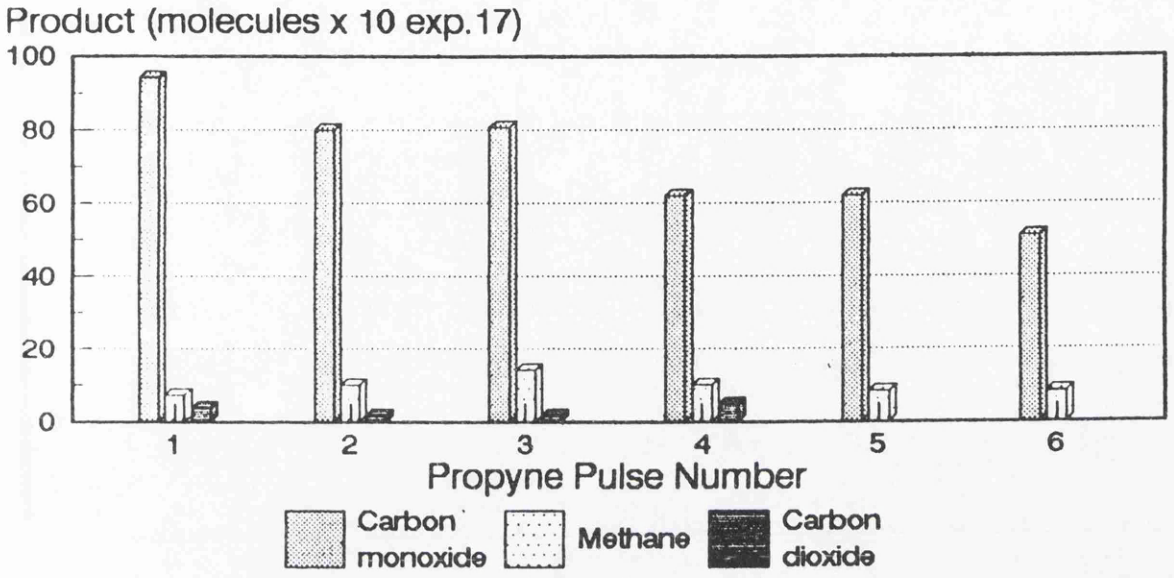


Figure 5.13b Carbon Balance for the Interaction of Pulses of C_3H_4 with a Pt/alumina Catalyst at 600°C.
(Catalyst weight = 0.2242 g).

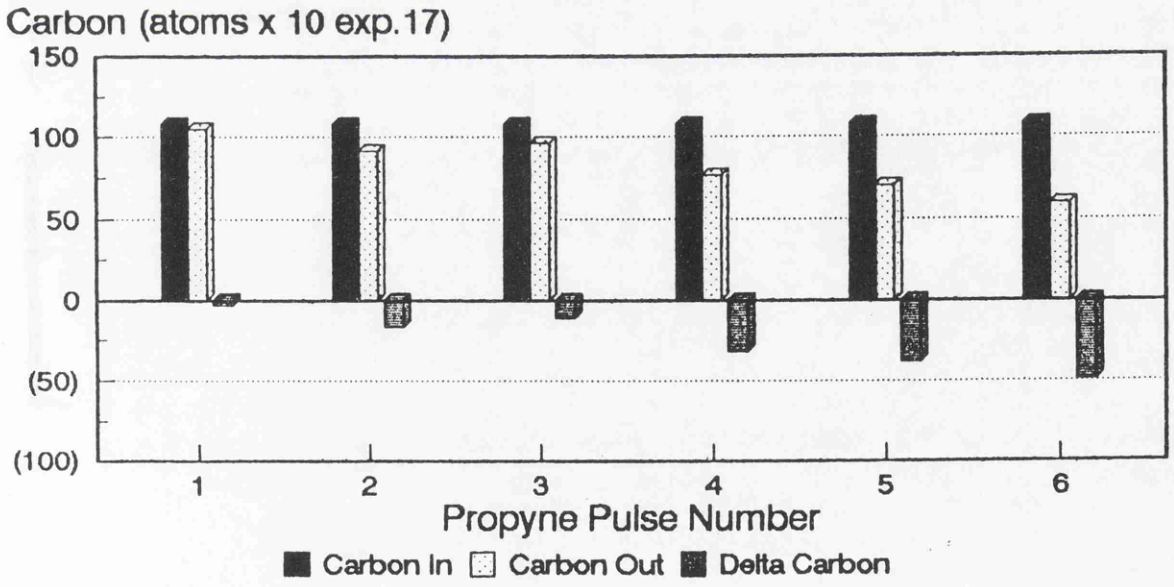


Table 5.16c Hydrogen Balance for the Interaction of Pulses of C_3H_4 with a Pt/alumina Catalyst at 600°C.
(Catalyst weight = 0.2242 g).

Hydrogen atoms x 10^{17}

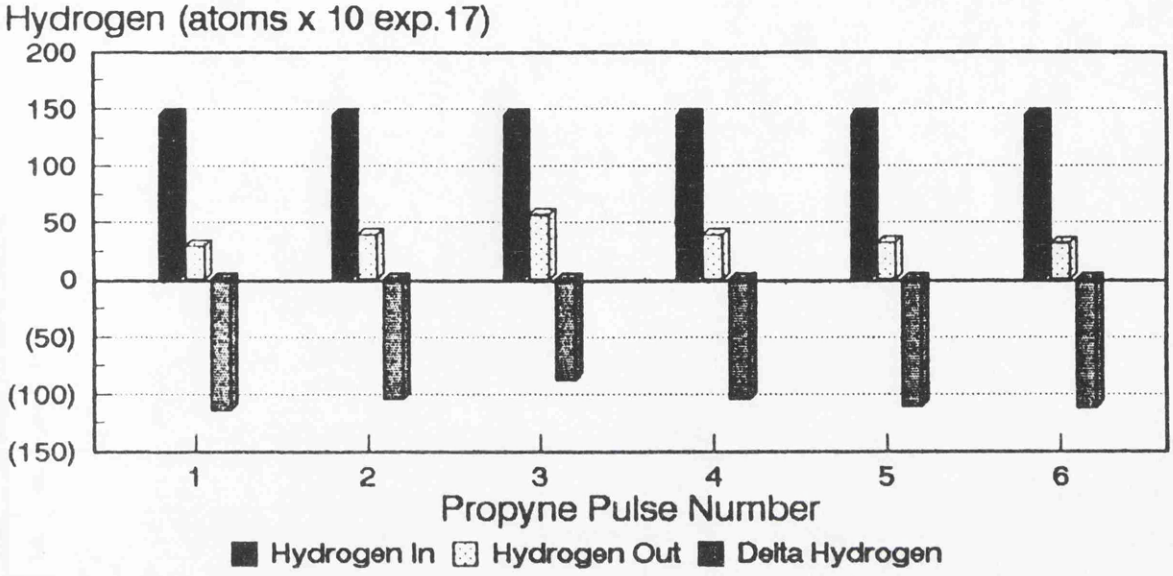
Pulse	Hydrogen In	Hydrogen Out	Delta Hydrogen
1 (C_3H_4)	144.0	28.8	-115.2
2 (C_3H_4)	144.0	39.2	-104.8
3 (C_3H_4)	144.0	56.4	-87.6
4 (C_3H_4)	144.0	39.2	-104.8
5 (C_3H_4)	144.0	32.8	-111.2
6 (C_3H_4)	144.0	32.0	-112.0

Total hydrogen lost to the catalyst = 635.6 x 10^{17} atoms.

Table 5.16d Ratio of Carbon:Hydrogen Lost to the Catalyst During the Interaction of Pulses of C_3H_4 with a Pt/alumina Catalyst at 600°C.
(Catalyst weight = 0.2242 g).

Pulse	1 (C_3H_4)	2 (C_3H_4)	3 (C_3H_4)	4 (C_3H_4)	5 (C_3H_4)	6 (C_3H_4)	Total
Ratio of C:H Lost to Catalyst	1:38	1:6	1:7	1:3	1:3	1:2	1:4

Figure 5.13c Hydrogen Balance for the Interaction of Pulses of C_3H_4 with a Pt/alumina Catalyst at 600°C.
(Catalyst weight = 0.2242 g).



Experiment C(K)APRY.01

Table 5.17a Product Distribution for the Interaction of Pulses of C_3H_4 with a Chromia/K/alumina Catalyst at 500°C.
(Catalyst weight = 0.2046 g; Pulse size = 36.0 x 10^{17} molecules).

Product molecules x 10^{17}

Pulse	CO	CH_4	CO_2	C_3H_6
1 (C_3H_4)	trace	trace	87.5	0.0
2 (C_3H_4)	1.2	1.4	55.5	0.0
3 (C_3H_4)	1.6	2.3	52.3	0.0
4 (C_3H_4)	11.4	15.1	4.2	0.0
5 (C_3H_4)	9.4	13.3	0.0	2.0
6 (C_3H_4)	8.3	12.5	0.0	2.4

Table 5.17b Carbon Balance for the Interaction of Pulses of C_3H_4 with a Chromia/K/alumina Catalyst at 500°C.
(Catalyst weight = 0.2046 g).

Carbon atoms x 10^{17}

Pulse	Carbon In	Carbon Out	Delta Carbon
1 (C_3H_4)	108.0	87.5	-20.5
2 (C_3H_4)	108.0	58.1	-49.9
3 (C_3H_4)	108.0	56.2	-51.8
4 (C_3H_4)	108.0	30.7	-77.3
5 (C_3H_4)	108.0	28.7	-79.3
6 (C_3H_4)	108.0	28.0	-80.0

Total carbon lost to the catalyst = 358.8 x 10^{17} atoms.

Experiment C(K)APRY.01

Figure 5.14a Product Distribution for the Interaction of Pulses of C_3H_4 with a Chromia/K/alumina Catalyst at 500°C.
(Catalyst weight = 0.2046 g; Pulse size = 36.0 x 10^{17} molecules).

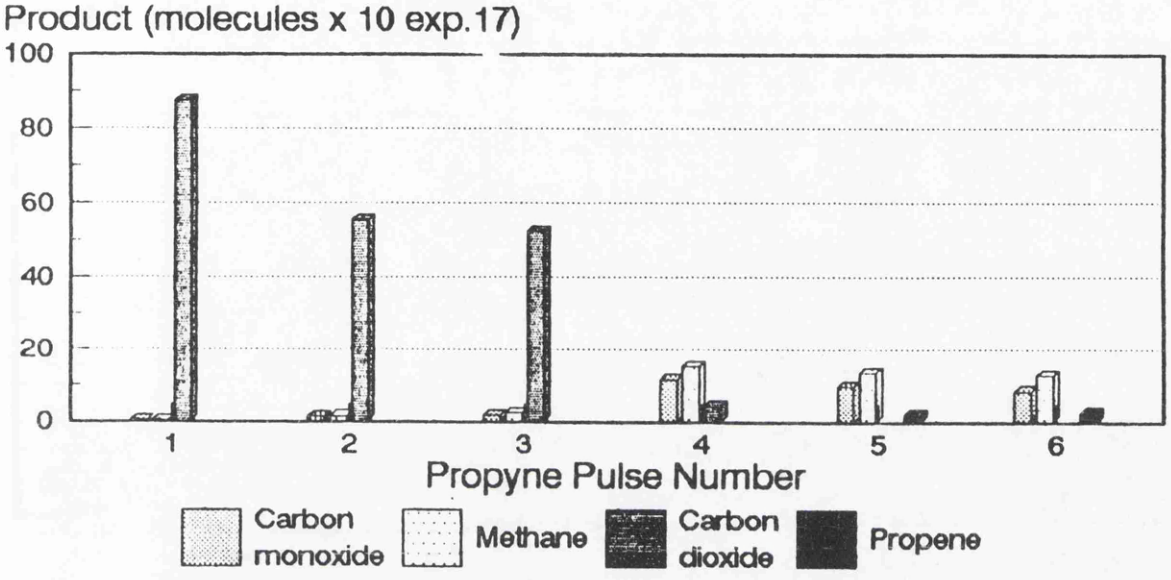


Figure 5.14b Carbon Balance for the Interaction of Pulses of C_3H_4 with a Chromia/K/alumina Catalyst at 500°C.
(Catalyst weight = 0.2046 g).

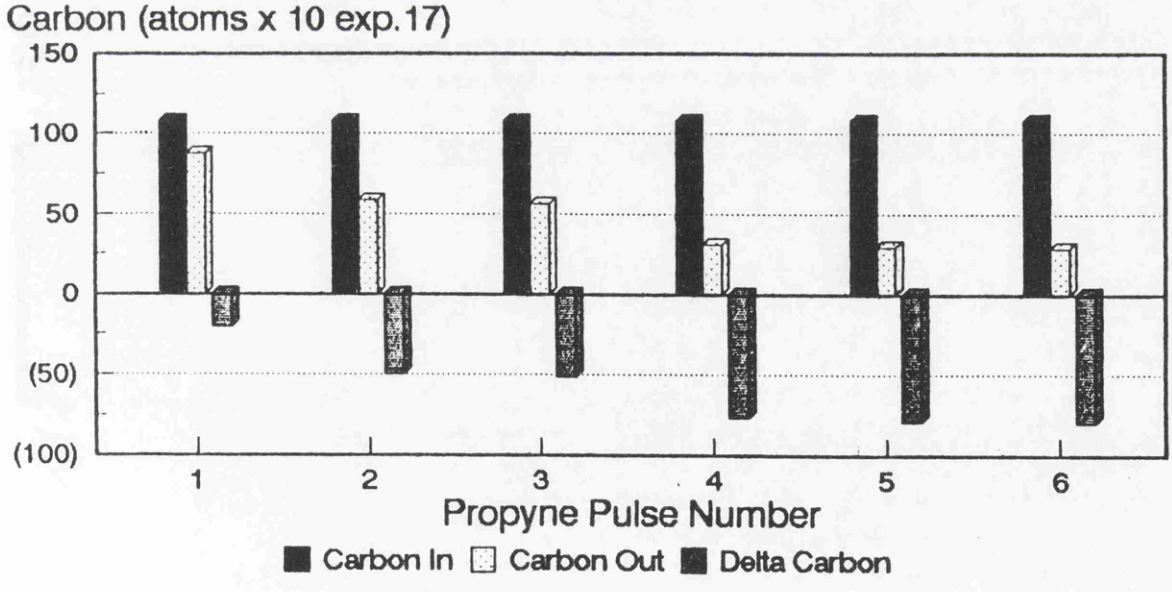


Table 5.17c Hydrogen Balance for the Interaction of Pulses of C_3H_4 with a Chromia/K/alumina Catalyst at 500°C.
(Catalyst weight = 0.2046 g).

Hydrogen atoms x 10^{17}

Pulse	Hydrogen In	Hydrogen Out	Delta Hydrogen
1 (C_3H_4)	144.0	trace	-144.0
2 (C_3H_4)	144.0	5.6	-138.4
3 (C_3H_4)	144.0	9.2	-134.8
4 (C_3H_4)	144.0	60.4	-83.6
5 (C_3H_4)	144.0	65.2	-78.8
6 (C_3H_4)	144.0	64.4	-79.6

Total hydrogen lost to the catalyst = 659.2 x 10^{17} atoms.

Table 5.17d Ratio of Carbon:Hydrogen Lost to the Catalyst During the Interaction of Pulses of C_3H_4 with a Chromia/K/alumina Catalyst at 500°C.
(Catalyst weight = 0.2046 g).

Pulse	1 (C_3H_4)	2 (C_3H_4)	3 (C_3H_4)	4 (C_3H_4)	5 (C_3H_4)	6 (C_3H_4)	Total
Ratio of C:H Lost to Catalyst	1:7	1:3	1:3	1:1	1:1	1:1	1:2

Figure 5.14c Hydrogen Balance for the Interaction of Pulses of C_3H_4 with a Chromia/K/alumina Catalyst at 500°C. (Catalyst weight = 0.2046 g).

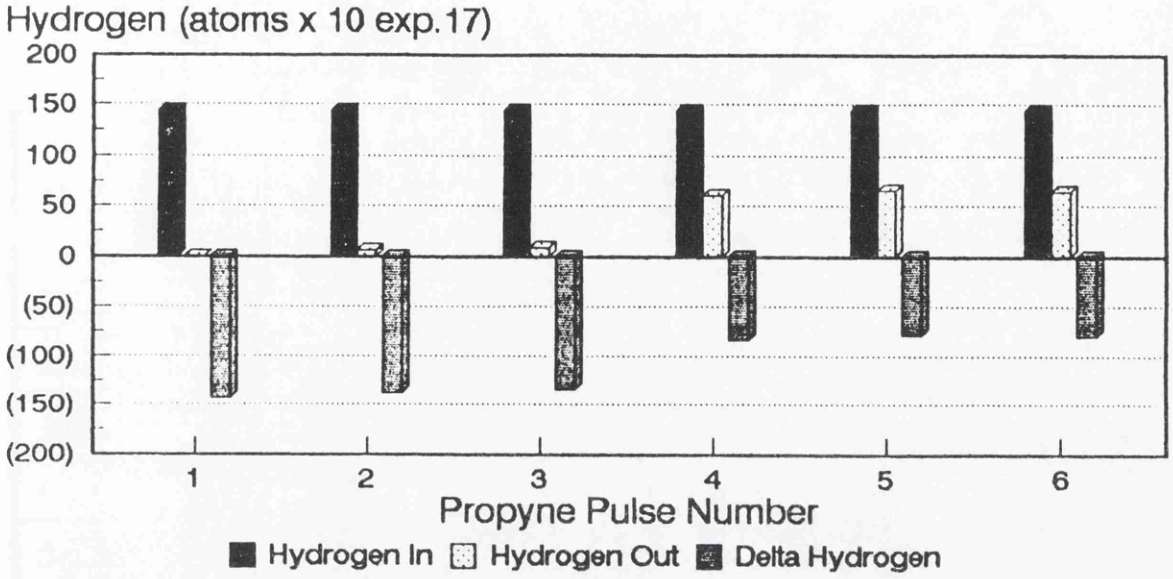


Table 5.17e Oxygen Balance for the Interaction of Dioxygen with the Used Chromia/K/alumina Catalyst at 500°C.
(Catalyst weight = 0.2046 g)

Molecules x 10^{17}

Pulse	O_2 In	O_2 Out	CO Out	CO_2 Out	O_2 Taken Up
1(O_2)	36.0	0.0	2.8	25.6	9.0
2(O_2)	36.0	0.0	2.3	23.8	11.0
3(O_2)	36.0	0.0	2.1	21.5	13.4
4(O_2)	36.0	0.0	1.7	17.6	17.6
5(O_2)	36.0	0.0	0.5	16.8	19.0
6(O_2)	36.0	0.9	0.0	13.5	21.6
7(O_2)	36.0	1.1	0.0	11.8	23.1
8(O_2)	36.0	1.1	0.0	9.1	25.8
9(O_2)	36.0	1.0	0.0	7.0	28.0
10(O_2)	36.0	2.6	0.0	4.0	29.4
11(O_2)	36.0	3.8	0.0	1.7	30.5
12(O_2)	36.0	6.7	0.0	0.4	28.9
13(O_2)	36.0	14.6	0.0	0.0	21.4
14(O_2)	36.0	14.1	0.0	0.0	21.9

Total carbon burnt off catalyst as CO or CO_2 = 162.2 x 10^{17} atoms.

Experiment C(K)APRY.02

Table 5.18a Product Distribution for the Interaction of Pulses of C_3H_4 with a Chromia/K/alumina Catalyst at 550°C.
(Catalyst weight = 0.2019 g; Pulse size = 36.0 x 10^{17} molecules).

Product molecules x 10^{17}

Pulse	CO	CH_4	CO_2	C_2H_6	C_3H_6
1 (C_3H_4)	47.1	35.0	25.4	0.0	0.0
2 (C_3H_4)	41.6	32.7	20.1	0.0	0.0
3 (C_3H_4)	33.9	31.3	4.9	0.0	0.0
4 (C_3H_4)	36.5	36.7	4.1	0.0	0.0
5 (C_3H_4)	14.1	27.1	3.4	0.2	1.6
6 (C_3H_4)	11.7	11.1	1.5	0.2	2.6

Table 5.18b Carbon Balance for the Interaction of Pulses of C_3H_4 with a Chromia/K/alumina Catalyst at 550°C.
(Catalyst weight = 0.2019 g).

Carbon atoms x 10^{17}

Pulse	Carbon In	Carbon Out	Delta Carbon
1 (C_3H_4)	108.0	107.5	-0.5
2 (C_3H_4)	108.0	94.4	-13.6
3 (C_3H_4)	108.0	70.1	-37.9
4 (C_3H_4)	108.0	77.3	-30.7
5 (C_3H_4)	108.0	49.8	-58.2
6 (C_3H_4)	108.0	32.5	-75.5

Total carbon lost to the catalyst = 216.4 x 10^{17} atoms.

Experiment C(K)APRY.02

Figure 5.15a Product Distribution for the Interaction of Pulses of C_3H_4 with a Chromia/K/alumina Catalyst at 550°C.
(Catalyst weight = 0.2019 g; Pulse size = 36.0 x 10^{17} molecules).

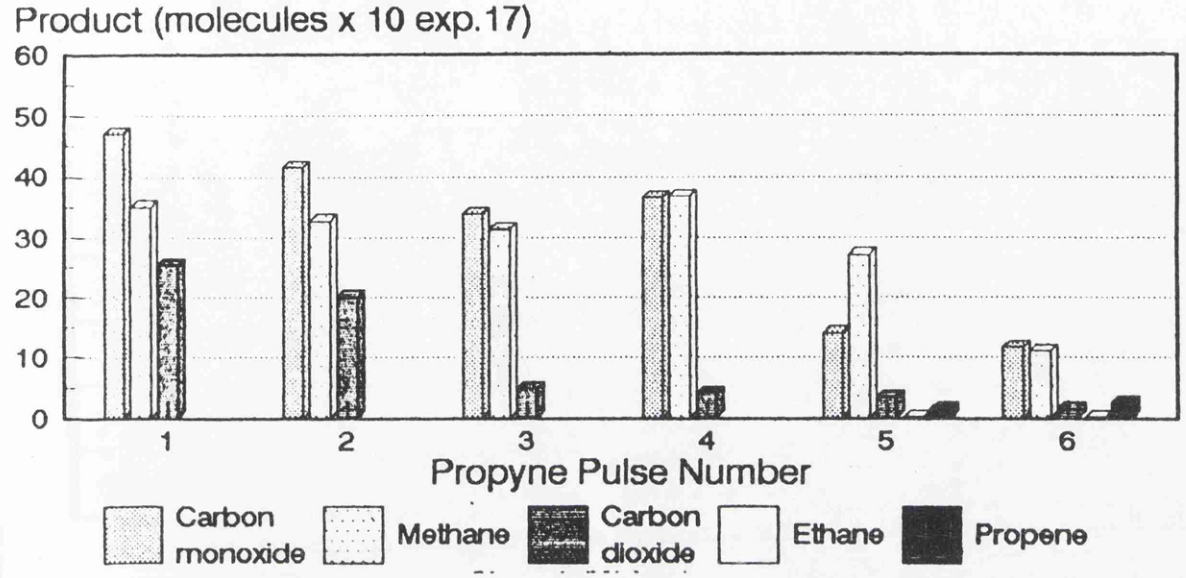


Figure 5.15b Carbon Balance for the Interaction of Pulses of C_3H_4 with a Chromia/K/alumina Catalyst at 550°C.
(Catalyst weight = 0.2019 g).

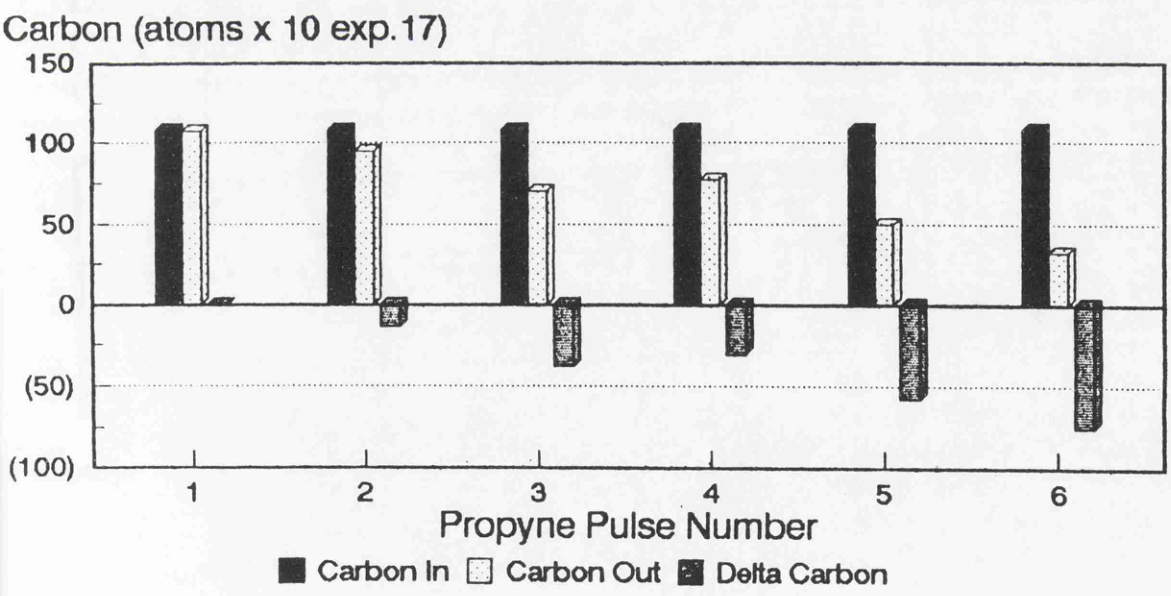


Table 5.18c Hydrogen Balance for the Interaction of Pulses of C_3H_4 with a Chromia/K/alumina Catalyst at 550°C.
(Catalyst weight = 0.2019 g).

Hydrogen atoms x 10^{17}

Pulse	Hydrogen In	Hydrogen Out	Delta Hydrogen
1 (C_3H_4)	144.0	140.0	-4.0
2 (C_3H_4)	144.0	130.8	-13.2
3 (C_3H_4)	144.0	125.2	-18.8
4 (C_3H_4)	144.0	146.8	2.8
5 (C_3H_4)	144.0	119.2	24.8
6 (C_3H_4)	144.0	61.2	82.8

Total hydrogen lost to the catalyst = 140.8 x 10^{17} atoms.

Table 5.18d Ratio of Carbon:Hydrogen Lost to the Catalyst During the Interaction of Pulses of C_3H_4 with a Chromia/K/alumina Catalyst at 550°C.
(Catalyst weight = 0.2019 g).

Pulse	1 (C_3H_4)	2 (C_3H_4)	3 (C_3H_4)	4 (C_3H_4)	5 (C_3H_4)	6 (C_3H_4)	Total
Ratio of C:H Lost to Catalyst	1:4	1:1	1:1	∞[a]	∞[a]	1:1	1:1

[a] ∞ means only carbon was lost to the catalyst.

Figure 5.15c Hydrogen Balance for the Interaction of Pulses of C_3H_4 with a Chromia/K/alumina Catalyst at 550°C.
(Catalyst weight = 0.2019 g).

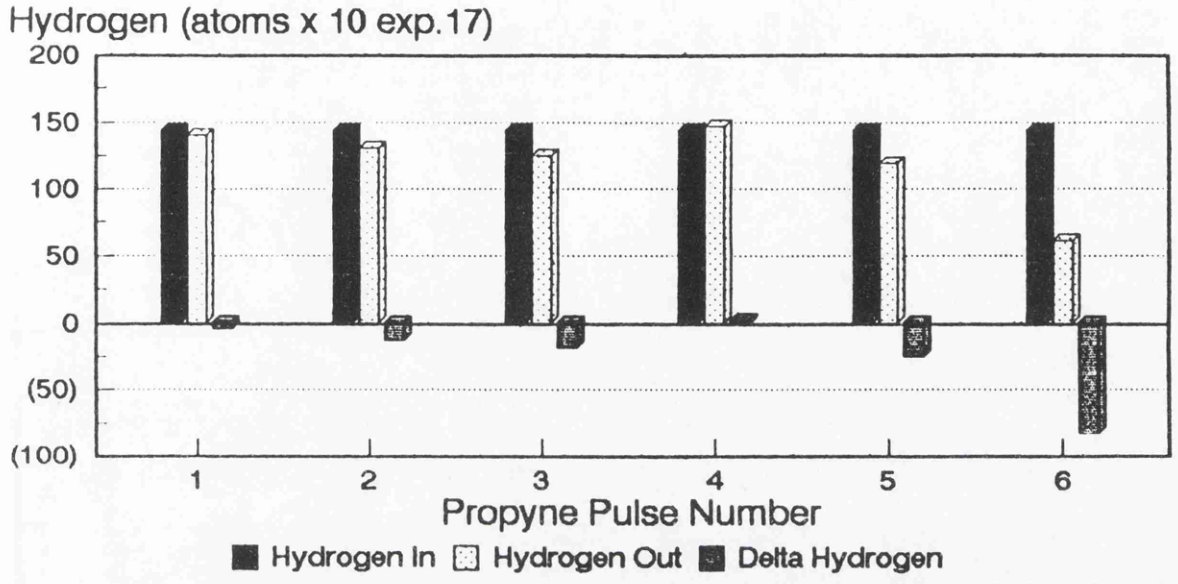


Table 5.18e Oxygen Balance for the Interaction of Dioxygen with the Used Chromia/K/alumina Catalyst at 550°C.
(Catalyst weight = 0.2019 g)

Molecules x 10^{17}

Pulse	O_2 In	O_2 Out	CO Out	CO_2 Out	O_2 Taken Up
1(O_2)	36.0	0.0	0.0	14.8	21.2
2(O_2)	36.0	0.0	0.5	15.0	20.8
3(O_2)	36.0	0.0	2.2	11.2	23.7
4(O_2)	36.0	0.0	2.1	8.8	26.2
5(O_2)	36.0	0.0	1.5	5.9	29.4
6(O_2)	36.0	1.7	0.0	5.1	29.2
7(O_2)	36.0	1.7	0.0	5.0	29.3
8(O_2)	36.0	1.8	0.0	2.3	31.9

Total carbon burnt off catalyst as CO or CO_2 = 74.4 x 10^{17} atoms.

Experiment C(K)APRY.03

Table 5.19a Product Distribution for the Interaction of Pulses of C_3H_4 with a Chromia/K/alumina Catalyst at 600°C.
(Catalyst weight = 0.1989 g; Pulse size = 36.0 x 10^{17} molecules).

Product molecules x 10^{17}

Pulse	CO	CH_4	CO_2	C_3H_6
1 (C_3H_4)	53.4	33.8	14.9	0.6
2 (C_3H_4)	45.3	32.0	7.4	0.9
3 (C_3H_4)	47.0	28.9	7.3	0.9
4 (C_3H_4)	43.7	29.2	4.8	1.0
5 (C_3H_4)	31.6	41.6	5.5	1.0
6 (C_3H_4)	53.4	21.3	8.0	1.6

Table 5.19b Carbon Balance for the Interaction of Pulses of C_3H_4 with a Chromia/K/alumina Catalyst at 600°C.
(Catalyst weight = 0.1989 g).

Carbon atoms x 10^{17}

Pulse	Carbon In	Carbon Out	Delta Carbon
1 (C_3H_4)	108.0	103.9	-4.1
2 (C_3H_4)	108.0	87.4	-20.6
3 (C_3H_4)	108.0	85.9	-22.1
4 (C_3H_4)	108.0	80.7	-27.3
5 (C_3H_4)	108.0	81.7	-26.3
6 (C_3H_4)	108.0	87.5	-20.5

Total carbon lost to the catalyst = 120.9 x 10^{17} atoms.

Experiment C(K)APRY.03

Figure 5.16a Product Distribution for the Interaction of Pulses of C_3H_4 with a Chromia/K/alumina Catalyst at 600°C.
(Catalyst weight = 0.1989 g; Pulse size = 36.0 x 10^{17} molecules).

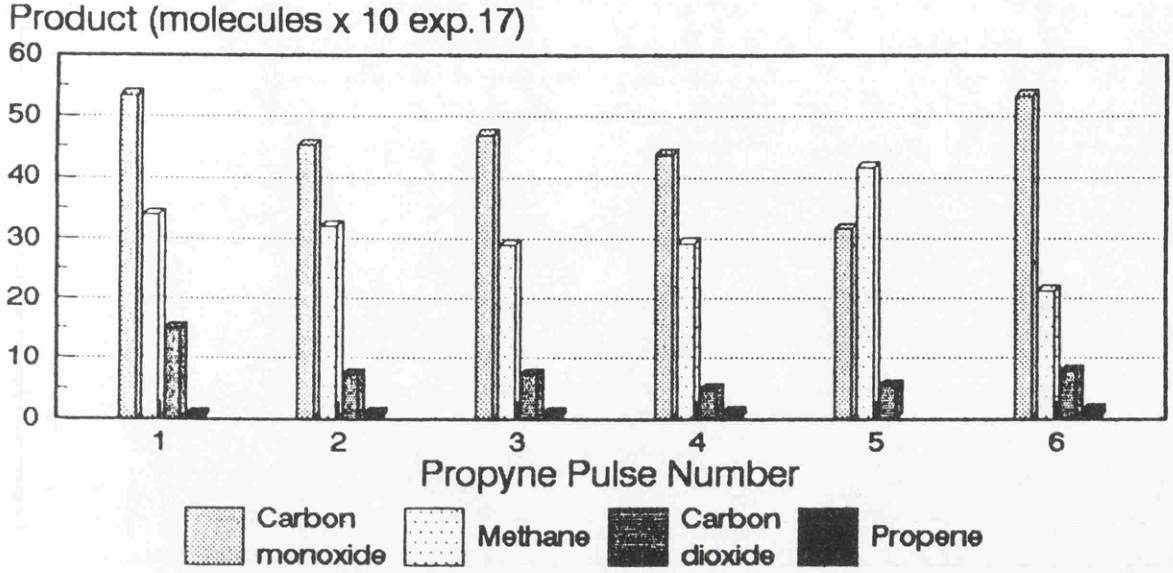


Figure 5.16b Carbon Balance for the Interaction of Pulses of C_3H_4 with a Chromia/K/alumina Catalyst at 600°C.
(Catalyst weight = 0.1989 g).

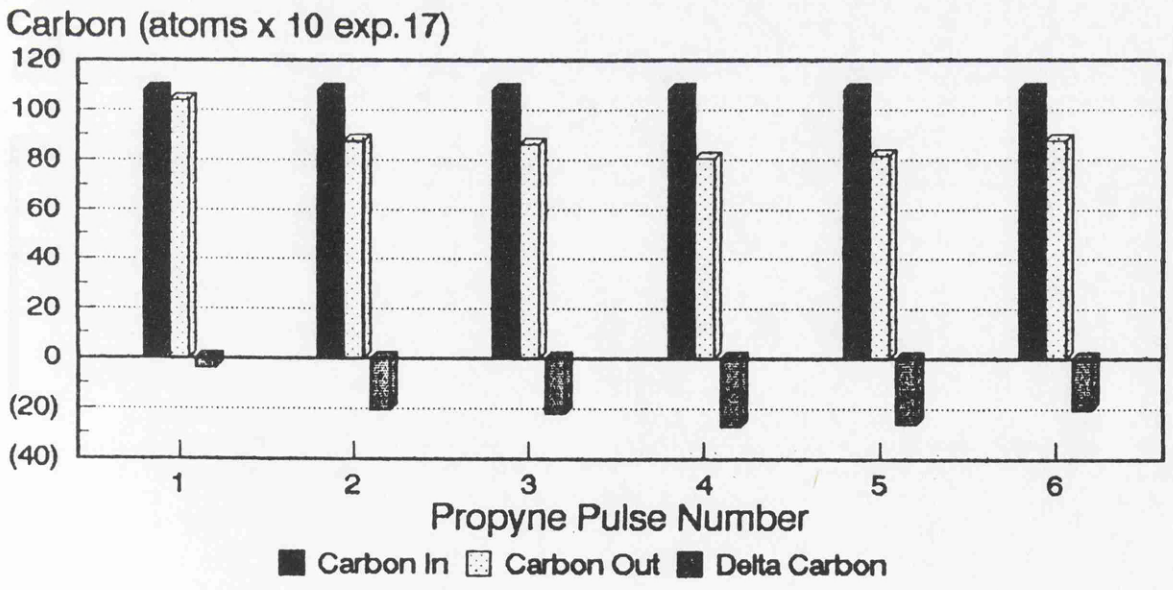


Table 5.19c Hydrogen Balance for the Interaction of Pulses of C_3H_4 with a Chromia/K/alumina Catalyst at 600°C.
(Catalyst weight = 0.1989 g).

Hydrogen atoms x 10^{17}

Pulse	Hydrogen In	Hydrogen Out	Delta Hydrogen
1 (C_3H_4)	144.0	138.8	-5.2
2 (C_3H_4)	144.0	133.4	-10.6
3 (C_3H_4)	144.0	121.0	-23.0
4 (C_3H_4)	144.0	122.8	-21.2
5 (C_3H_4)	144.0	172.4	28.4
6 (C_3H_4)	144.0	94.8	-49.2

Total hydrogen lost to the catalyst = 80.8 x 10^{17} atoms.

Table 5.19d Ratio of Carbon:Hydrogen Lost to the Catalyst During the Interaction of Pulses of C_3H_4 with a Chromia/K/alumina Catalyst at 600°C.
(Catalyst weight = 0.1989 g).

Pulse	1 (C_3H_4)	2 (C_3H_4)	3 (C_3H_4)	4 (C_3H_4)	5 (C_3H_4)	6 (C_3H_4)	Total
Ratio of C:H Lost to Catalyst	1:1	1:1	1:1	1:1	∞[a]	1:2	1:1

[a] ∞ means only carbon was lost to the catalyst.

Figure 5.16c Hydrogen Balance for the Interaction of Pulses of C_3H_4 with a Chromia/K/alumina Catalyst at 600°C. (Catalyst weight = 0.1989 g).

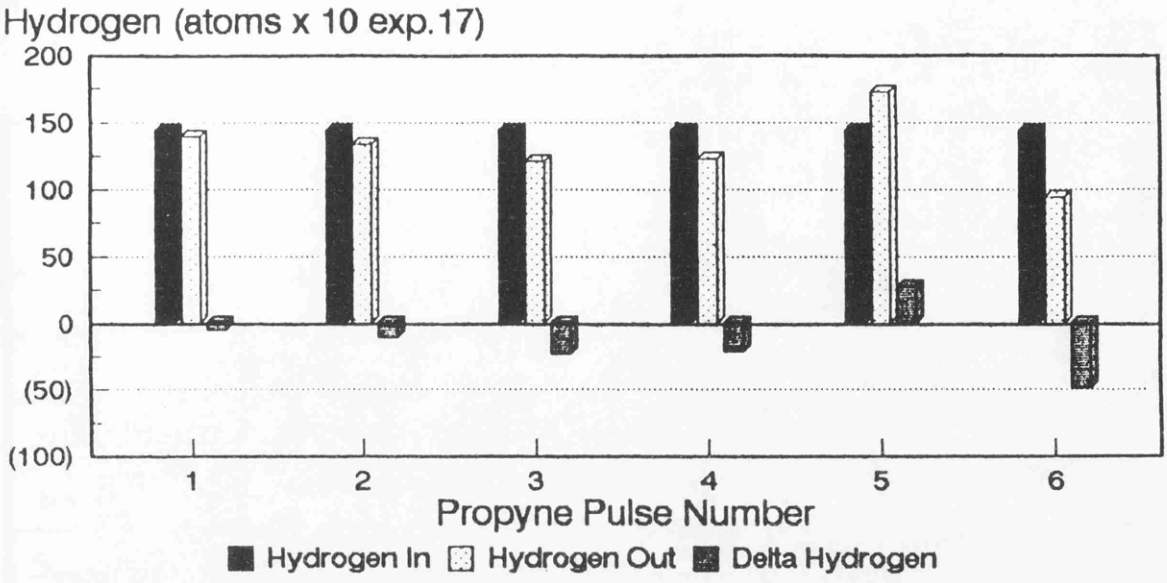


Table 5.19e Oxygen Balance for the Interaction of Dioxygen with the Used Chromia/K/alumina Catalyst at 600°C.
(Catalyst weight = 0.1989 g)

Molecules x 10^{17}

Pulse	O_2 In	O_2 Out	CO Out	CO_2 Out	O_2 Taken Up
1(O_2)	36.0	0.0	8.8	15.1	16.5
2(O_2)	36.0	0.0	4.6	13.7	20.0
3(O_2)	36.0	0.0	3.2	13.6	20.8
4(O_2)	36.0	3.6	0.0	10.5	21.9
5(O_2)	36.0	4.3	0.0	8.3	23.4
6(O_2)	36.0	4.1	0.0	8.0	23.9
7(O_2)	36.0	3.9	0.0	5.6	26.5
8(O_2)	36.0	4.3	0.0	2.1	29.6
9(O_2)	36.0	3.1	0.0	2.2	30.7
10(O_2)	36.0	5.0	0.0	0.0	31.0
11(O_2)	36.0	4.5	0.0	0.0	31.5
12(O_2)	36.0	8.3	0.0	0.0	27.7
13(O_2)	36.0	11.2	0.0	0.0	24.8

Total carbon burnt off catalyst as CO or CO_2 = 95.7 x 10^{17} atoms.

Experiment C(K)ADPRY.01

Table 5.20a Product Distribution for the Interaction of Pulses of C_3H_4 with a Deuterium Reduced Chromia/K/alumina Catalyst at 600°C. (Catalyst weight = 0.2131 g; Pulse size = 36.0 x 10^{17} molecules).

Product molecules x 10^{17}

Pulse	CO	CX_4	CO_2	C_3X_6
1 (C_3H_4)	17.5	14.8	45.2	0.0
2 (C_3H_4)	26.6	32.4	6.5	1.8
3 (C_3H_4)	27.0	31.4	4.1	2.1

Table 5.20b Carbon Balance for the Interaction of Pulses of C_3H_4 with a Deuterium Reduced Chromia/K/alumina Catalyst at 600°C. (Catalyst weight = 0.2131 g).

Carbon atoms x 10^{17}

Pulse	Carbon In	Carbon Out	Delta Carbon
1 (C_3H_4)	108.0	77.5	-30.5
2 (C_3H_4)	108.0	70.9	-37.1
3 (C_3H_4)	108.0	68.8	-39.2

Total carbon lost to the catalyst = 106.8 x 10^{17} atoms.

Experiment C(K)ADPRY.01

Figure 5.17a Product Distribution for the Interaction of Pulses of C_3H_4 with a Deuterium Reduced Chromia/K/alumina Catalyst at 600°C. (Catalyst weight = 0.2131 g; Pulse size = 36.0 x 10^{17} molecules).

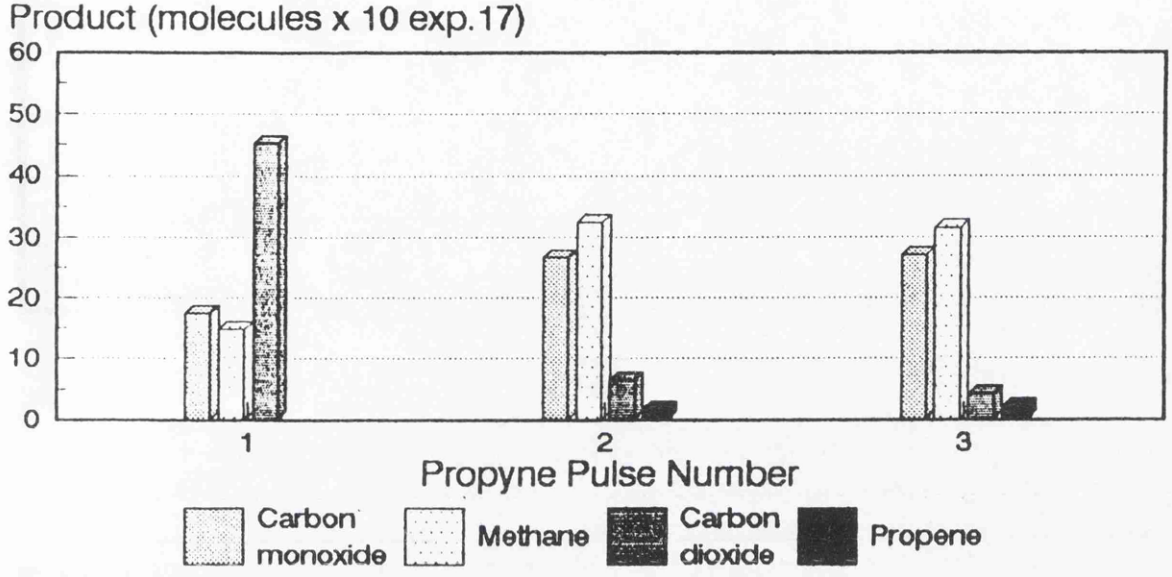


Figure 5.17b Carbon Balance for the Interaction of Pulses of C_3H_4 with a Deuterium Reduced Chromia/K/alumina Catalyst at 600°C. (Catalyst weight = 0.2131 g).

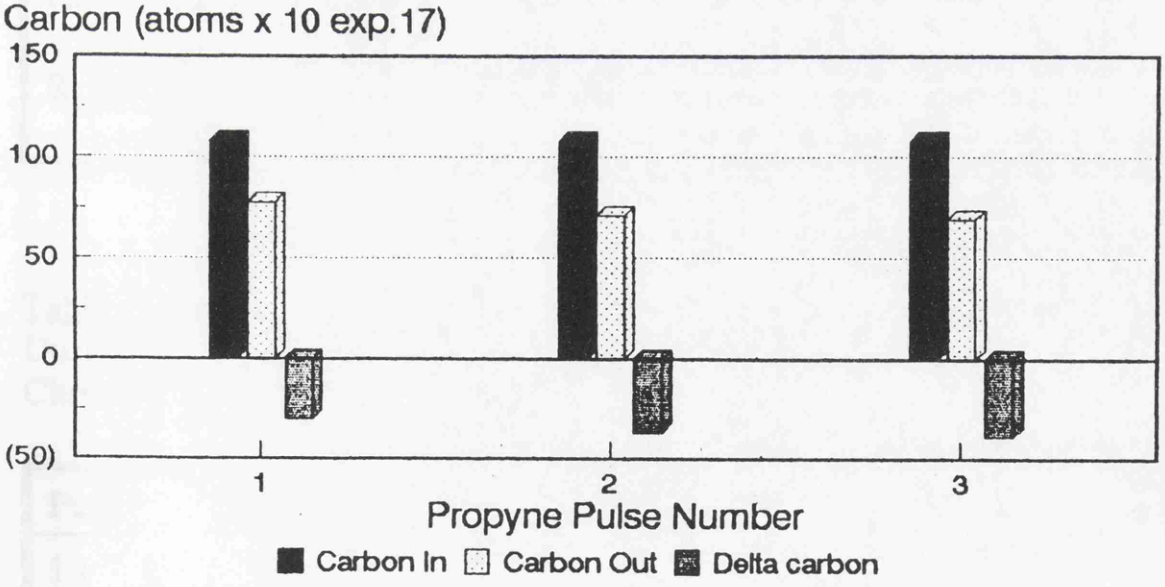


Table 5.20c Hydrogen Balance for the Interaction of Pulses of C_3H_4 with a Deuterium Reduced Chromia/K/alumina Catalyst at 600°C. (Catalyst weight = 0.2131 g).

Hydrogen atoms x 10^{17}

Pulse	Hydrogen In	Hydrogen Out	Delta Hydrogen
1 (C_3H_4)	144.0	59.2	-84.8
2 (C_3H_4)	144.0	140.4	-3.6
3 (C_3H_4)	144.0	138.2	-5.8

Total carbon lost to the catalyst = 94.2 x 10^{17} atoms.

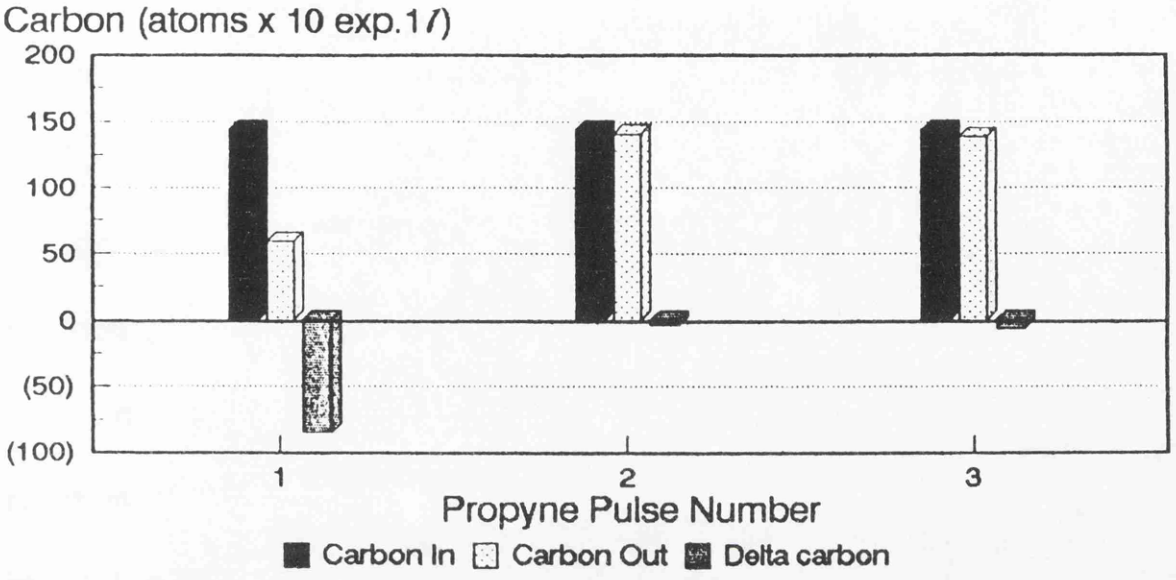
Table 5.20d Ratio of Carbon:Hydrogen Lost to the Catalyst During the Interaction of Pulses of C_3H_4 with a Deuterium Reduced Chromia/K/alumina Catalyst at 600°C.
(Catalyst weight = 0.2131 g).

Pulse	1 (C_3H_4)	2 (C_3H_4)	6 (C_3H_4)	Total
Ratio of C:H Lost to Catalyst	1:3	1:0.1	1:0.1	1:1

Table 5.20e Calculated Ratio of Isotopic Methanes Produced During the Interaction of Pulses of C_3H_4 with a Deuterium Reduced Chromia/K/alumina Catalyst at 600°C.

Pulse	CD_4	CD_3H	CD_2H_2	CDH_3	CH_4
1 (C_3H_4)	0	11	89	0	0
2 (C_3H_4)	23	38	39	0	0
3 (C_3H_4)	16	38	46	0	0

Figure 5.17c Hydrogen Balance for the Interaction of Pulses of C_3H_4 with a Deuterium Reduced Chromia/K/alumina Catalyst at 600°C. (Catalyst weight = 0.2131 g).



5.4 TRANSHYDROGENATION

Experiments were carried out to determine whether the catalysts had any activity towards transhydrogenation. This was done by passing a 1:1 mixture of propyne:propane over a reduced catalyst charge using the gas adsorption apparatus, described in Section 3.3, following the reaction procedure outlined in Section 3.4.

In order to follow the hydrogen during the transhydrogenation reaction most of the experiments involved the use of perdeutero propane in a 1:1 mix with propyne. Two other transhydrogenation experiments were carried out. The first involved the use of a 1:1 mix of unlabelled propane:propyne. This experiment was designed to determine what would happen if there was no deuterium/hydrogen isotope effect present. The second involved doubling the pulse size of the 1:1 mix of unlabelled propane:propyne. This experiment was designed to see what effect quantity of reactants had on the product distribution.

The results of these experiments are given in Tables 5.21a - 5.29d and Figures 5.18a - 5.26c.

Note

1. The first two, or three, letters of the code refers to the catalyst used:-

   PA = platinum/alumina

   C(K)A = chromia/alumina promoted with potassium.

2. The remaining group of letters refers to the gases used in the experiment:-

   DTH = a 1:1 mix of deuterated propane and unlabelled propyne

   TH = a 1:1 mix of unlabelled propane and unlabelled propyne.

3. Finally, the two digits at the end of the code are the experiment number for a particular catalyst and experiment type as described by the letters of the code.

Transhydrogenation Experiments

Experiment	Catalyst	Temperature	Gases
PADTH.01	Pt/alumina	500°C	1:1 C_3H_4:C_3D_8
PADTH.02	Pt/alumina	550°C	1:1 C_3H_4:C_3D_8
PADTH.03	Pt/alumina	600°C	1:1 C_3H_4:C_3D_8
C(K)ADTH.01	Chromia/K/alumina	400°C	1:1 C_3H_4:C_3D_8
C(K)ADTH.02	Chromia/K/alumina	500°C	1:1 C_3H_4:C_3D_8
C(K)ADTH.03	Chromia/K/alumina	550°C	1:1 C_3H_4:C_3D_8
C(K)ADTH.04	Chromia/K/alumina	600°C	1:1 C_3H_4:C_3D_8
C(K)ATH.01	Chromia/K/alumina	550°C	1:1 C_3H_4:C_3H_8
C(K)ATH.02	Chromia/K/alumina	550°C	1:1 C_3H_4:C_3H_8

Experiment PADTH.01

Table 5.21a Product Distribution for the Interaction of Pulses of 1: 1 C_3H_4:C_3D_8 with a Pt/alumina Catalyst at 500°C. (Catalyst weight = 0.2199 g; Pulse size = 36.0 x 10^{17} molecules).

Product molecules x 10^{17}

Pulse	CO	CX_4	CO_2	C_3X_8
1(C_3H_4/C_3D_8)	36.1	54.9	0.7	3.9
2(C_3H_4/C_3D_8)	12.2	42.3	0.4	9.9
3(C_3H_4/C_3D_8)	14.6	29.0	0.0	12.6
4(C_3H_4/C_3D_8)	12.8	19.8	0.0	11.9
5(C_3H_4/C_3D_8)	16.4	15.0	0.0	12.8
6(C_3H_4/C_3D_8)	15.9	15.8	0.0	12.6

Table 5.21b Carbon Balance for the Interaction of Pulses of 1:1 C_3H_4:C_3D_8 with a Pt/alumina Catalyst at 500°C. (Catalyst weight = 0.2199 g).

Carbon atoms x 10^{17}

Pulse	Carbon In	Carbon Out	Delta Carbon
1(C_3H_4/C_3D_8)	108.0	103.4	-4.6
2(C_3H_4/C_3D_8)	108.0	84.6	-23.4
3(C_3H_4/C_3D_8)	108.0	81.4	-26.6
4(C_3H_4/C_3D_8)	108.0	68.3	-39.7
5(C_3H_4/C_3D_8)	108.0	69.8	-38.2
6(C_3H_4/C_3D_8)	108.0	69.5	-38.5

Total carbon lost to the catalyst = 171.0 x 10^{17} atoms.

Experiment PADTH.01

Figure 5.18a Product Distribution for the Interaction of Pulses of 1: 1 C_3H_4:C_3D_8 with a Pt/alumina Catalyst at 500°C.
(Catalyst weight = 0.2199 g; Pulse size = 36.0 x 10^{17} molecules).

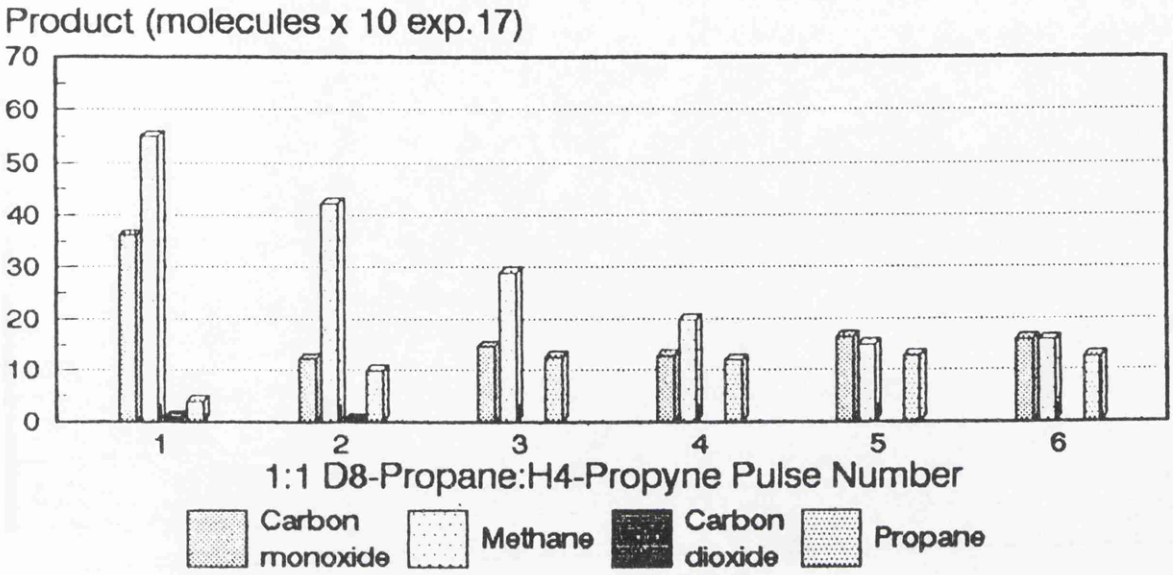


Figure 5.18b Carbon Balance for the Interaction of Pulses of 1:1 C_3H_4:C_3D_8 with a Pt/alumina Catalyst at 500°C.
(Catalyst weight = 0.2199 g).

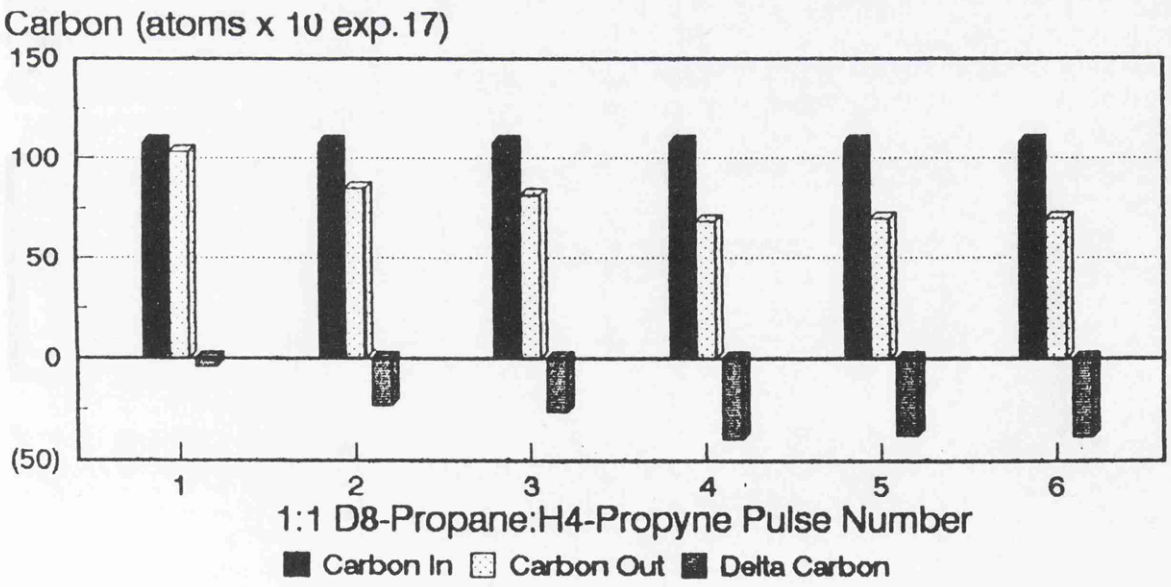


Table 5.21c Hydrogen Balance for the Interaction of Pulses of 1:1 C_3H_4:C_3D_8 with a Pt/alumina Catalyst at 500°C.
(Catalyst weight = 0.2199 g).

Hydrogen atoms x 10^{17}

Pulse	Hydrogen In	Hydrogen Out	Delta Hydrogen
1(C_3H_4/C_3D_8)	216.0	250.8	34.8
2(C_3H_4/C_3D_8)	216.0	248.8	32.4
3(C_3H_4/C_3D_8)	216.0	216.8	0.8
4(C_3H_4/C_3D_8)	216.0	174.4	-41.6
5(C_3H_4/C_3D_8)	216.0	162.4	-53.6
6(C_3H_4/C_3D_8)	216.0	164.0	-52.0

Total hydrogen lost to the catalyst = 79.2 x 10^{17} atoms.

Table 5.21d Ratio of Carbon:Hydrogen Lost to the Catalyst During the Interaction of Pulses of 1:1 C_3H_4:C_3D_8 with a Pt/alumina Catalyst at 500°C.
(Catalyst weight = 0.2199 g).

Pulse	1	2	3	4	5	6	Total
Ratio of C:H Lost to Catalyst	∞[a]	∞[a]	∞[a]	1:1	1:1	1:1	2:1

[a] ∞ means that only carbon was lost to the catalyst.

Figure 5.18c Hydrogen Balance for the Interaction of Pulses of 1:1 C_3H_4:C_3D_8 with a Pt/alumina Catalyst at 500°C.
(Catalyst weight = 0.2199 g).

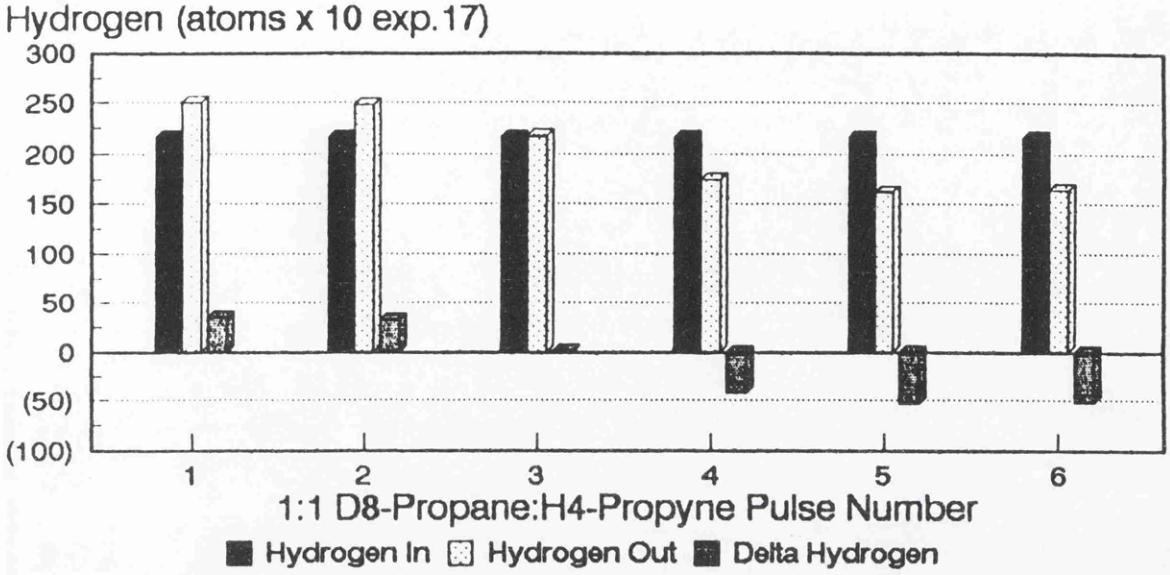


Table 5.21e Oxygen Balance for the Interaction of Dioxygen with the Used Pt/alumina Catalyst at 500°C.
(Catalyst weight = 0.2199 g)

Molecules x 10^{17}

Pulse	O_2 In	O_2 Out	CO Out	CO_2 Out	O_2 Taken Up
1(O_2)	36.0	0.0	3.1	32.2	2.2
2(O_2)	36.0	0.0	2.5	31.7	3.0
3(O_2)	36.0	0.0	2.4	27.2	7.6
4(O_2)	36.0	0.0	1.6	25.5	9.7
5(O_2)	36.0	7.2	0.0	20.7	8.1
6(O_2)	36.0	12.5	0.0	12.1	11.4

Total carbon burnt off catalyst as CO or CO_2 = 159.0 x 10^{17} atoms.

Table 5.21f Calculated ratio of Isotopic Methanes Produced During the Interaction of 1:1 C_3H_4:C_3D_8 with a Pt/alumina Catalyst at 500°C.

Pulse	CD_4	CD_3H	CD_2H_2	CDH_3	CH_4
1(C_3H_4/C_3D_8)	0	1	6	12	81
2(C_3H_4/C_3D_8)	0	2	7	20	71
3(C_3H_4/C_3D_8)	0	3	12	24	61
4(C_3H_4/C_3D_8)	0	4	16	20	60
5(C_3H_4/C_3D_8)	0	5	20	15	60
6(C_3H_4/C_3D_8)	0	5	14	24	57

Table 5.21g Normalised Mass Spectra for Unreacted Propane During the Interaction of 1:1 C_3H_4:C_3D_8 with a Pt/alumina Catalyst at 500°C.

m/z	Pulse 1 (C_3H_4/C_3D_8)	Pulse 2 (C_3H_4/C_3D_8)	Pulse 3 (C_3H_4/C_3D_8)	Pulse 4 (C_3H_4/C_3D_8)	Pulse 5 (C_3H_4/C_3D_8)	Pulse 6 (C_3H_4/C_3D_8)
36	0.44	0.31	0.26	0.13	0.10	0.03
37	0.44	0.77	0.48	0.27	0.15	0.03
38	1.11	1.77	1.13	0.77	0.60	0.53
39	1.78	3.46	2.00	1.20	0.70	0.50
40	1.89	3.92	2.48	1.57	1.12	1.13
41	2.89	4.92	3.13	2.07	1.40	1.25
42	2.48	4.62	3.22	2.30	1.80	1.72
43	1.56	2.62	1.57	0.93	0.60	0.38
44	1.22	2.92	1.57	1.00	0.62	0.78
45	1.78	2.92	1.57	1.10	0.80	0.88
46	1.56	2.92	1.52	1.00	0.70	0.81
47	1.56	2.77	1.48	0.93	0.60	0.59
48	1.71	2.40	1.63	1.22	0.90	0.87
49	1.78	2.15	1.78	1.40	1.25	1.19
50	0.98	1.26	1.17	0.97	0.89	0.86
51	1.00	1.00	1.00	1.00	1.00	1.00
52	0.00	0.00	0.00	0.00	0.00	0.00

Experiment PADTH.02

Table 5.22a Product Distribution for the Interaction of Pulses of 1: 1 C_3H_4:C_3D_8 with a Pt/alumina Catalyst at 550°C. (Catalyst weight = 0.2167 g; Pulse size = 36.0 x 10^{17} molecules).

Product molecules x 10^{17}

Pulse	CO	CX_4	CO_2
1(C_3H_4/C_3D_8)	63.2	27.0	2.3
2(C_3H_4/C_3D_8)	49.8	37.5	2.2
3(C_3H_4/C_3D_8)	52.5	45.2	0.8
4(C_3H_4/C_3D_8)	52.9	41.9	0.8
5(C_3H_4/C_3D_8)	52.9	40.2	0.8
6(C_3H_4/C_3D_8)	49.0	42.1	0.7

Table 5.22b Carbon Balance for the Interaction of Pulses of 1:1 C_3H_4:C_3D_8 with a Pt/alumina Catalyst at 550°C. (Catalyst weight = 0.2167 g).

Carbon atoms x 10^{17}

Pulse	Carbon In	Carbon Out	Delta Carbon
1(C_3H_4/C_3D_8)	108.0	92.5	-15.5
2(C_3H_4/C_3D_8)	108.0	89.5	-18.5
3(C_3H_4/C_3D_8)	108.0	98.5	-9.5
4(C_3H_4/C_3D_8)	108.0	95.6	-12.4
5(C_3H_4/C_3D_8)	108.0	93.9	-14.1
6(C_3H_4/C_3D_8)	108.0	91.8	-16.2

Total carbon lost to the catalyst = 86.2 x 10^{17} atoms.

Experiment PADTH.02

Figure 5.19a Product Distribution for the Interaction of Pulses of 1: 1 C_3H_4:C_3D_8 with a Pt/alumina Catalyst at 550°C. (Catalyst weight = 0.2167 g; Pulse size = 36.0 x 10^{17} molecules).

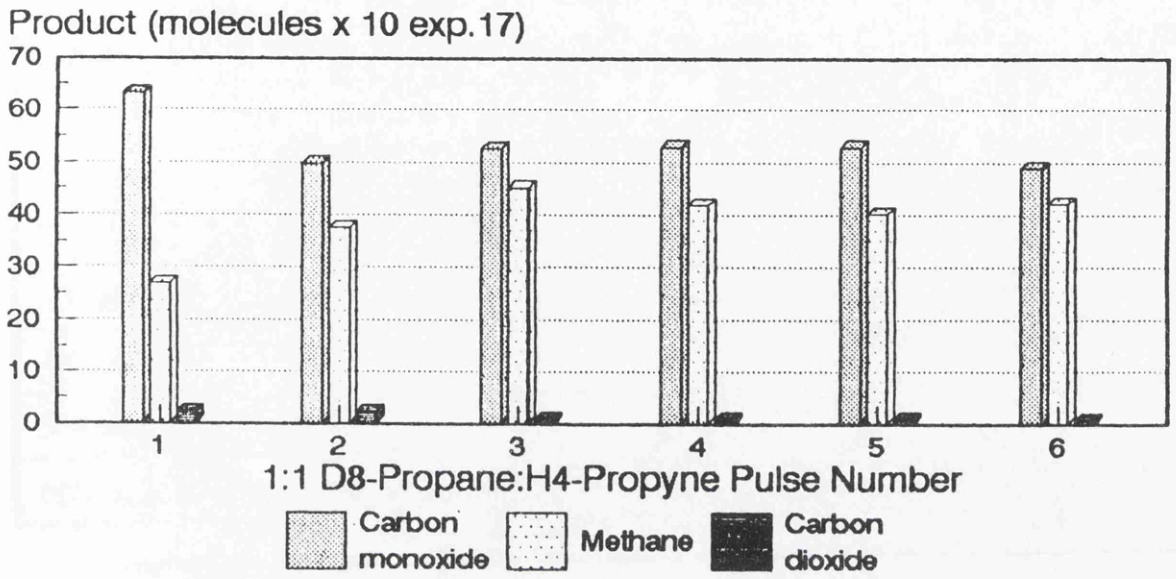


Figure 5.19b Carbon Balance for the Interaction of Pulses of 1:1 C_3H_4:C_3D_8 with a Pt/alumina Catalyst at 550°C. (Catalyst weight = 0.2167 g).

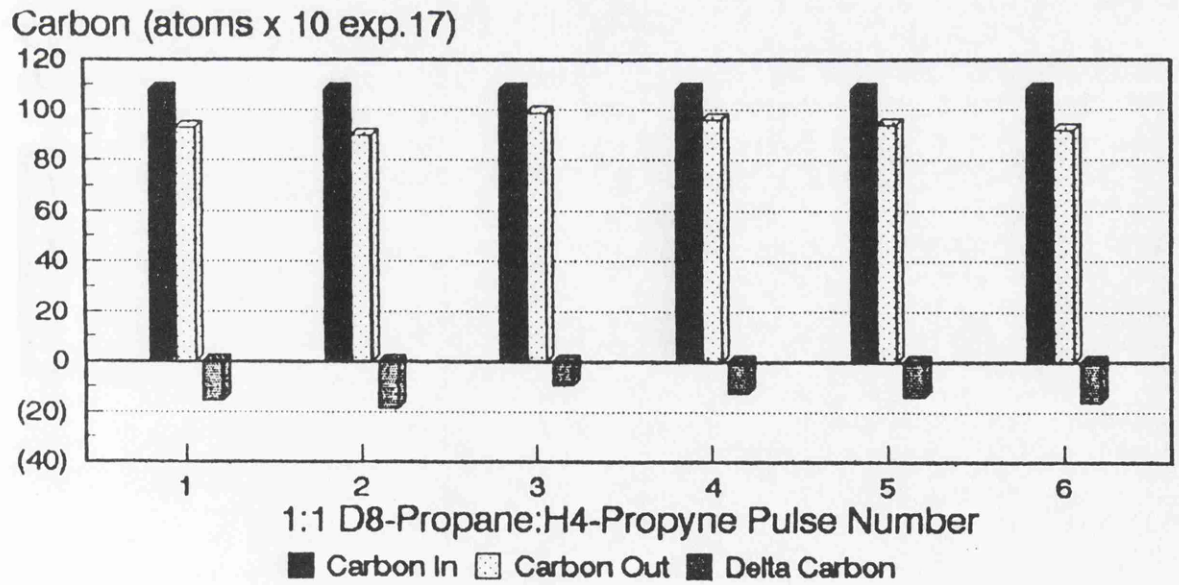


Table 5.22c Hydrogen Balance for the Interaction of Pulses of 1:1 C_3H_4:C_3D_8 with a Pt/alumina Catalyst at 550°C.
(Catalyst weight = 0.2167 g).

Hydrogen atoms x 10^{17}

Pulse	Hydrogen In	Hydrogen Out	Delta Hydrogen
1(C_3H_4/C_3D_8)	216.0	108.0	-108.0
2(C_3H_4/C_3D_8)	216.0	150.0	-66.0
3(C_3H_4/C_3D_8)	216.0	180.8	-35.2
4(C_3H_4/C_3D_8)	216.0	167.6	-48.4
5(C_3H_4/C_3D_8)	216.0	160.8	-55.2
6(C_3H_4/C_3D_8)	216.0	168.4	-47.6

Total hydrogen lost to the catalyst = 360.4 x 10^{17} atoms.

Table 5.22d Ratio of Carbon:Hydrogen Lost to the Catalyst During the Interaction of Pulses of 1:1 C_3H_4:C_3D_8 with a Pt/alumina Catalyst at 550°C.
(Catalyst weight = 0.2167 g).

Pulse	1	2	3	4	5	6	Total
Ratio of C:H Lost to Catalyst	1:7	1:4	1:4	1:4	1:4	1:3	1:4

Figure 5.19c Hydrogen Balance for the Interaction of Pulses of 1:1 C_3H_4:C_3D_8 with a Pt/alumina Catalyst at 550°C.
(Catalyst weight = 0.2167 g).

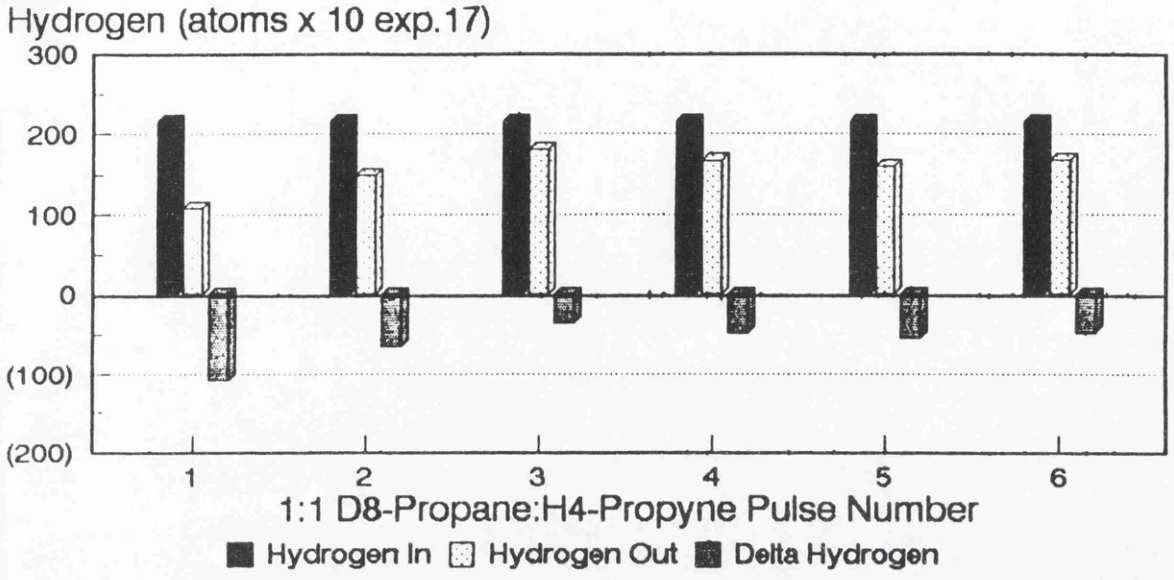


Table 5.22e Oxygen Balance for the Interaction of Dioxygen with the Used Pt/alumina Catalyst at 550°C.
(Catalyst weight = 0.2167 g)

Molecules x 10^{17}

Pulse	O_2 In	O_2 Out	CO Out	CO_2 Out	O_2 Taken Up
1(O_2)	36.0	0.0	0.0	23.9	14.0
2(O_2)	36.0	0.0	0.0	21.7	16.1
3(O_2)	36.0	36.0	0.0	0.0	0.0
4(O_2)	36.0	36.0	0.0	0.0	0.0
5(O_2)	36.0	36.0	0.0	0.0	0.0
6(O_2)	36.0	36.0	0.0	0.0	0.0

Total carbon burnt off catalyst as CO or CO_2 = 45.6 x 10^{17} atoms.

Table 5.22f Calculated ratio of Isotopic Methanes Produced During the Interaction of 1:1 C_3H_4:C_3D_8 with a Pt/alumina Catalyst at 550°C.

Pulse	CD_4	CD_3H	CD_2H_2	CDH_3	CH_4
1(C_3H_4/C_3D_8)	0	2	51	0	47
2(C_3H_4/C_3D_8)	2	4	30	12	52
3(C_3H_4/C_3D_8)	2	3	29	24	42
4(C_3H_4/C_3D_8)	2	6	33	29	30
5(C_3H_4/C_3D_8)	2	8	35	29	26
6(C_3H_4/C_3D_8)	2	10	34	31	23

Experiment PADTH.03

Table 5.23a Product Distribution for the Interaction of Pulses of 1: 1 C_3H_4:C_3D_8 with a Pt/alumina Catalyst at 600°C. (Catalyst weight = 0.2095 g; Pulse size = 36.0 x 10^{17} molecules).

Product molecules x 10^{17}

Pulse	CO	CX_4	CO_2
1(C_3H_4/C_3D_8)	61.9	31.8	1.6
2(C_3H_4/C_3D_8)	63.0	28.6	0.0
3(C_3H_4/C_3D_8)	54.7	34.4	0.0
4(C_3H_4/C_3D_8)	48.4	41.6	0.7
5(C_3H_4/C_3D_8)	51.2	28.1	0.0
6(C_3H_4/C_3D_8)	50.2	33.4	0.7
7(C_3H_4/C_3D_8)	45.8	36.2	0.7
8(C_3H_4/C_3D_8)	40.4	33.3	0.6

Table 5.23b Carbon Balance for the Interaction of Pulses of 1:1 C_3H_4:C_3D_8 with a Pt/alumina Catalyst at 600°C. (Catalyst weight = 0.2095 g).

Carbon atoms x 10^{17}

Pulse	Carbon In	Carbon Out	Delta Carbon
1(C_3H_4/C_3D_8)	108.0	95.3	-12.7
2(C_3H_4/C_3D_8)	108.0	91.6	-16.4
3(C_3H_4/C_3D_8)	108.0	89.1	-18.9
4(C_3H_4/C_3D_8)	108.0	90.7	-17.3
5(C_3H_4/C_3D_8)	108.0	79.3	-28.7
6(C_3H_4/C_3D_8)	108.0	84.3	-23.7
7(C_3H_4/C_3D_8)	108.0	82.7	-25.3
8(C_3H_4/C_3D_8)	108.0	74.3	-33.7

Total carbon lost to the catalyst = 176.7 x 10^{17} atoms.

Experiment PADTH.03

Figure 5.20a Product Distribution for the Interaction of Pulses of 1: 1 C_3H_4:C_3D_8 with a Pt/alumina Catalyst at 600°C. (Catalyst weight = 0.2095 g; Pulse size = 36.0 x 10^{17} molecules).

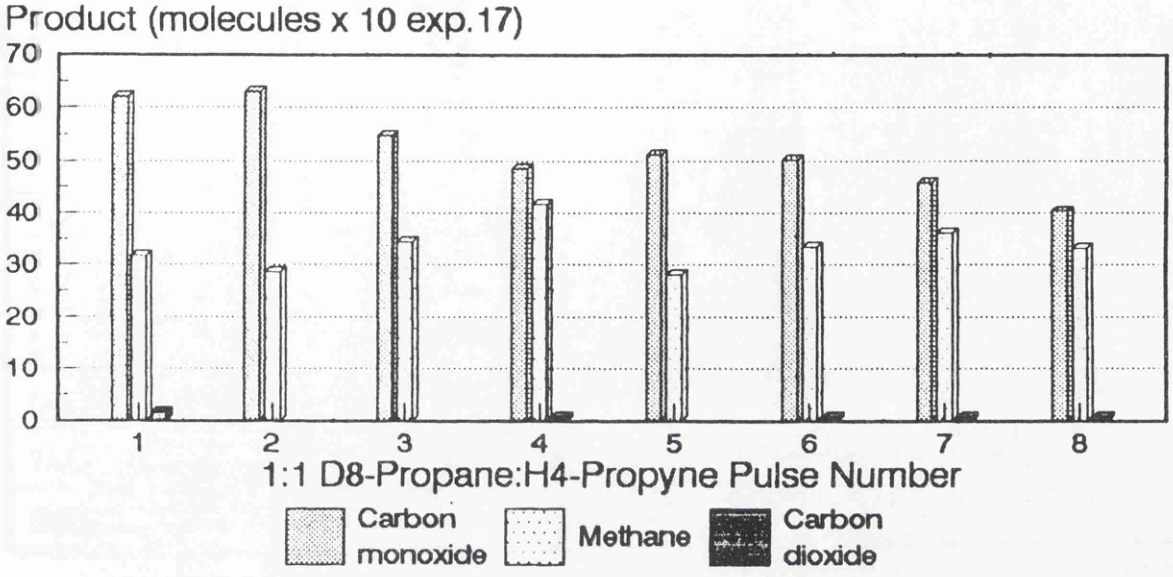


Figure 5.20b Carbon Balance for the Interaction of Pulses of 1:1 C_3H_4:C_3D_8 with a Pt/alumina Catalyst at 600°C. (Catalyst weight = 0.2095 g).

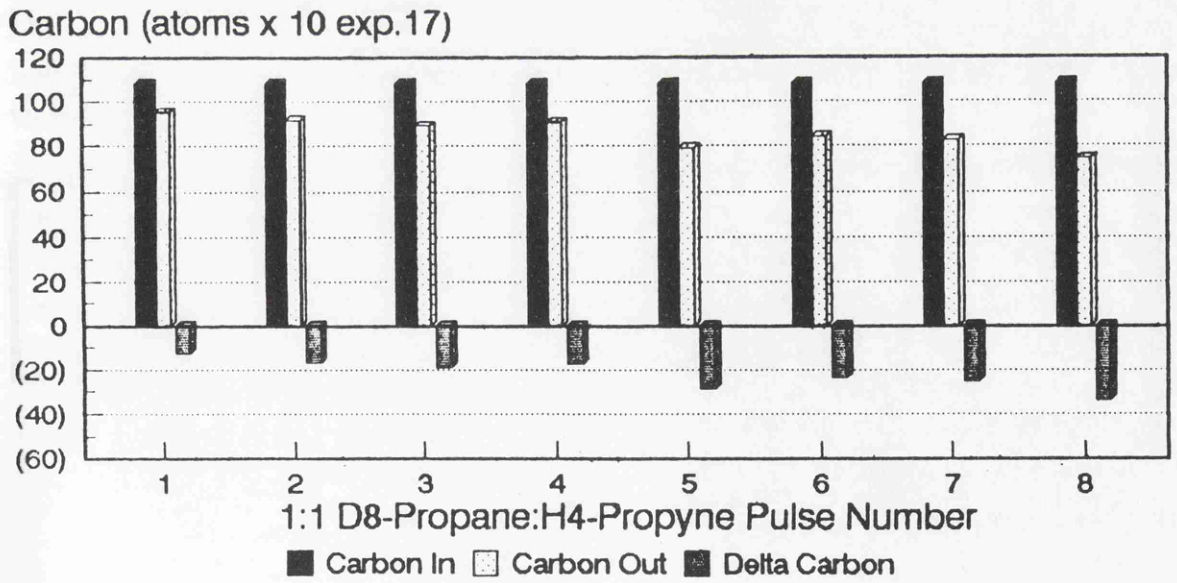


Table 5.23c Hydrogen Balance for the Interaction of Pulses of 1:1 C_3H_4:C_3D_8 with a Pt/alumina Catalyst at 600°C.
(Catalyst weight = 0.2095 g).

Hydrogen atoms x 10^{17}

Pulse	Hydrogen In	Hydrogen Out	Delta Hydrogen
1(C_3H_4/C_3D_8)	216.0	127.2	-88.8
2(C_3H_4/C_3D_8)	216.0	114.4	-101.6
3(C_3H_4/C_3D_8)	216.0	137.6	-78.4
4(C_3H_4/C_3D_8)	216.0	166.4	-49.6
5(C_3H_4/C_3D_8)	216.0	112.4	-103.6
6(C_3H_4/C_3D_8)	216.0	133.6	-82.4
7(C_3H_4/C_3D_8)	216.0	144.8	-71.2
8(C_3H_4/C_3D_8)	216.0	133.2	-82.8

Total hydrogen lost to the catalyst = 658.4 x 10^{17} atoms.

Table 5.23d Ratio of Carbon:Hydrogen Lost to the Catalyst During the Interaction of Pulses of 1:1 C_3H_4:C_3D_8 with a Pt/alumina Catalyst at 600°C.
(Catalyst weight = 0.2095 g).

Pulse	1	2	3	4	5	6	7	8	Total
Ratio of C:H Lost to Catalyst	1:7	1:6	1:4	1:3	1:4	1:3	1:3	1:2	1:4

Figure 5.20c Hydrogen Balance for the Interaction of Pulses of 1:1 C_3H_4:C_3D_8 with a Pt/alumina Catalyst at 600°C.
(Catalyst weight = 0.2095 g).

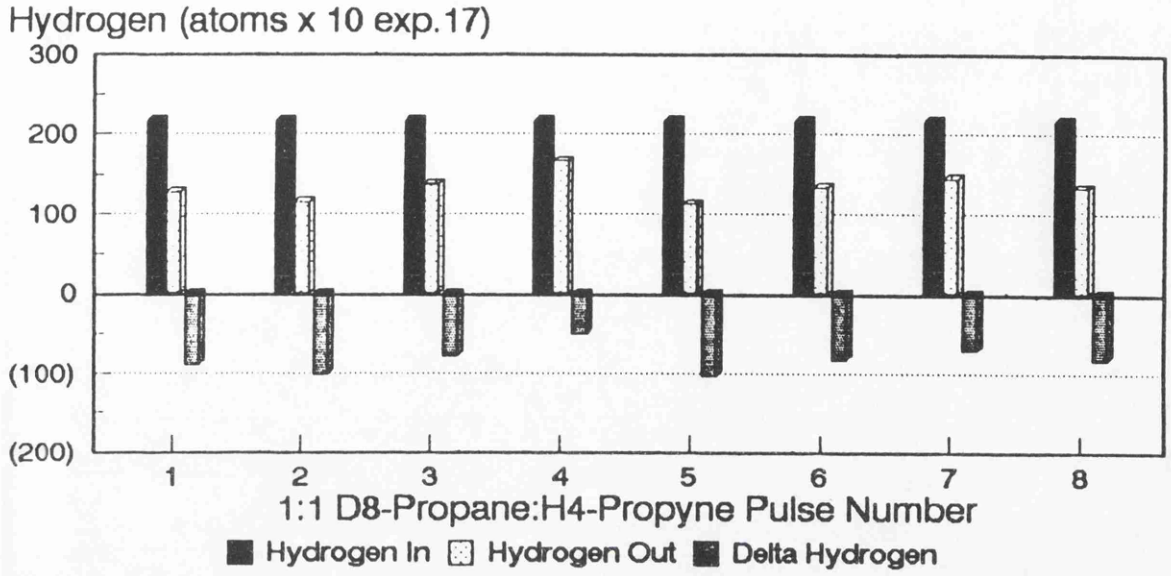


Table 5.23e Oxygen Balance for the Interaction of Dioxygen with the Used Pt/alumina Catalyst at 600°C.
(Catalyst weight = 0.2095 g)

Molecules x 10^{17}

Pulse	O_2 In	O_2 Out	CO Out	CO_2 Out	O_2 Taken Up
1(O_2)	36.0	5.1	0.0	20.6	10.3
2(O_2)	36.0	7.1	0.0	17.5	11.4
3(O_2)	36.0	22.1	0.0	9.8	4.1
4(O_2)	36.0	36.0	0.0	0.0	0.0
5(O_2)	36.0	36.0	0.0	0.0	0.0
6(O_2)	36.0	36.0	0.0	0.0	0.0

Total carbon burnt off catalyst as CO or CO_2 = 47.9 x 10^{17} atoms.

Table 5.23f Calculated Ratio of Isotopic Methanes Produced During the Interaction of 1:1 C_3H_4:C_3D_8 with a Pt/alumina Catalyst at 600°C.

Pulse	CD_4	CD_3H	CD_2H_2	CDH_3	CH_4
1(C_3H_4/C_3D_8)	0	2	43	0	55
2(C_3H_4/C_3D_8)	2	3	35	17	43
3(C_3H_4/C_3D_8)	2	5	33	28	32
4(C_3H_4/C_3D_8)	2	8	35	30	25
5(C_3H_4/C_3D_8)	2	11	40	28	19
6(C_3H_4/C_3D_8)	3	14	39	30	14
7(C_3H_4/C_3D_8)	4	16	40	25	15
8(C_3H_4/C_3D_8)	4	18	27	40	11

Experiment C(K)ADTH.01

Table 5.24a Product Distribution for the Interaction of Pulses of 1: 1 C_3H_4:C_3D_8 with a Chromia/K/alumina Catalyst at 400°C. (Catalyst weight = 0.2114 g; Pulse size = 36.0 x 10^{17} molecules).

Product molecules x 10^{17}

Pulse	CO	CX_4	CO_2	C_3X_8
1(C_3H_4/C_3D_8)	6.4	6.2	36.3	4.1
2(C_3H_4/C_3D_8)	2.3	8.0	3.9	15.7
3(C_3H_4/C_3D_8)	1.8	8.4	0.8	17.5
4(C_3H_4/C_3D_8)	4.9	6.1	0.8	17.3
5(C_3H_4/C_3D_8)	4.6	5.7	0.8	18.3
6(C_3H_4/C_3D_8)	3.1	7.1	0.3	18.0

Table 5.24b Carbon Balance for the Interaction of Pulses of 1:1 C_3H_4:C_3D_8 with a Chromia/K/alumina Catalyst at 400°C. (Catalyst weight = 0.2114 g).

Carbon atoms x 10^{17}

Pulse	Carbon In	Carbon Out	Delta Carbon
1(C_3H_4/C_3D_8)	108.0	81.7	-26.3
2(C_3H_4/C_3D_8)	108.0	61.3	-46.7
3(C_3H_4/C_3D_8)	108.0	63.5	-44.5
4(C_3H_4/C_3D_8)	108.0	63.7	-44.3
5(C_3H_4/C_3D_8)	108.0	66.0	-42.0
6(C_3H_4/C_3D_8)	108.0	64.5	-43.5

Total carbon lost to the catalyst = 247.3 x 10^{17} atoms.

Experiment C(K)ADTH.01

Figure 5.21a Product Distribution for the Interaction of Pulses of 1: 1 C_3H_4:C_3D_8 with a Chromia/K/alumina Catalyst at 400°C. (Catalyst weight = 0.2114 g; Pulse size = 36.0 x 10^{17} molecules).

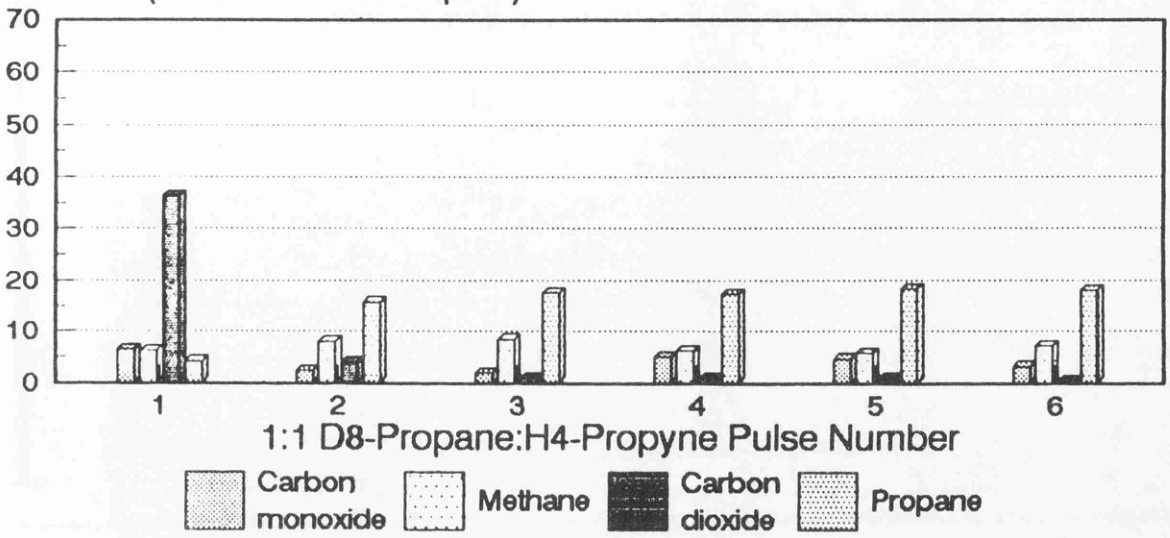


Figure 5.21b Carbon Balance for the Interaction of Pulses of 1:1 C_3H_4:C_3D_8 with a Chromia/K/alumina Catalyst at 400°C. (Catalyst weight = 0.2114 g).

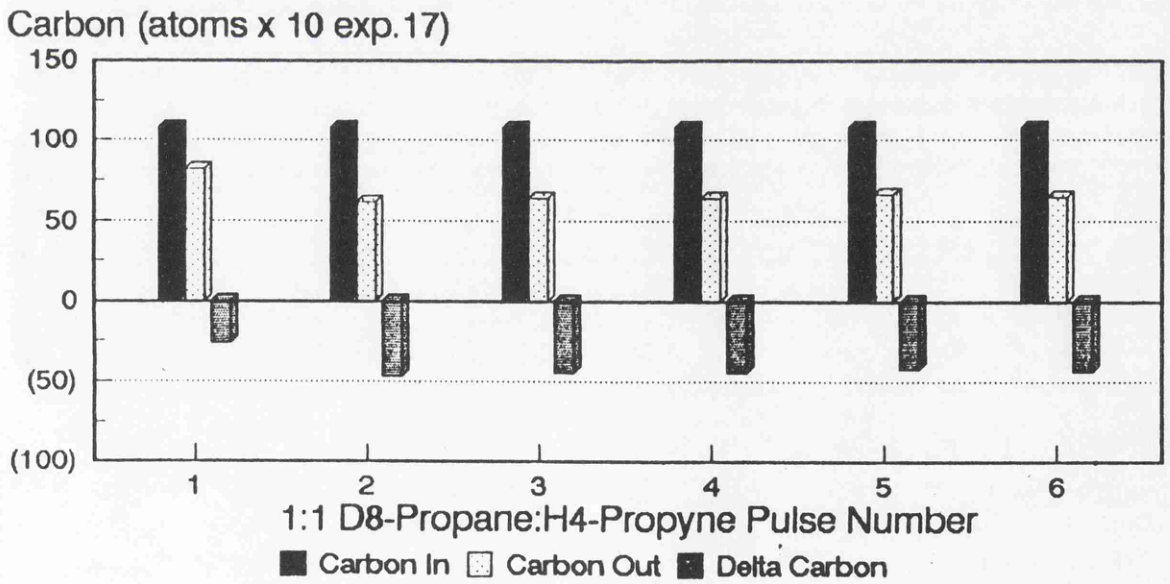


Table 5.24c Hydrogen Balance for the Interaction of Pulses of 1:1 C_3H_4:C_3D_8 with a Chromia/K/alumina Catalyst at 400°C. (Catalyst weight = 0.2114 g).

Hydrogen atoms x 10^{17}

Pulse	Hydrogen In	Hydrogen Out	Delta Hydrogen
1(C_3H_4/C_3D_8)	216.0	57.6	-158.4
2(C_3H_4/C_3D_8)	216.0	157.6	-58.4
3(C_3H_4/C_3D_8)	216.0	173.6	-42.4
4(C_3H_4/C_3D_8)	216.0	162.8	-53.2
5(C_3H_4/C_3D_8)	216.0	169.2	-46.8
6(C_3H_4/C_3D_8)	216.0	172.4	-43.6

Total hydrogen lost to the catalyst = 247.3 x 10^{17} atoms.

Table 5.24d Ratio of Carbon:Hydrogen Lost to the Catalyst During the Interaction of Pulses of 1:1 C_3H_4:C_3D_8 with a Chromia/K/alumina Catalyst at 400°C. (Catalyst weight = 0.2114 g).

Pulse	1	2	3	4	5	6	Total
Ratio of C:H Lost to Catalyst	1:6	1:1	1:1	1:1	1:1	1:1	1:2

Figure 5.21c Hydrogen Balance for the Interaction of Pulses of 1:1 C_3H_4:C_3D_8 with a Chromia/K/alumina Catalyst at 400°C. (Catalyst weight = 0.2114 g).

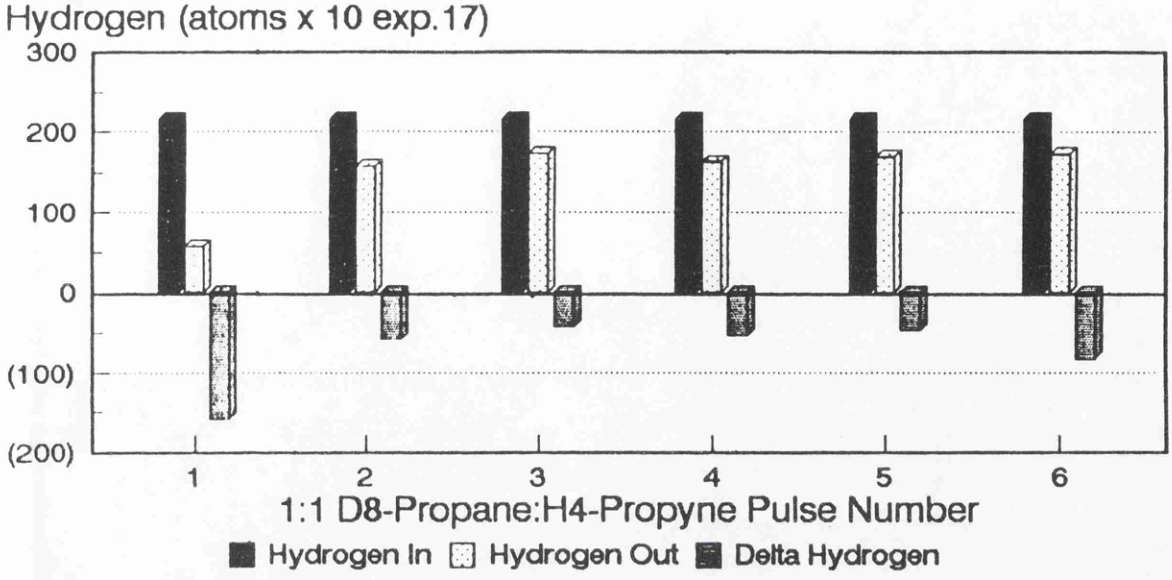


Table 5.24e Oxygen Balance for the Interaction of Dioxygen with the Used Chromia/K/alumina Catalyst at 400°C.
(Catalyst weight = 0.2114 g)

Molecules x 10^{17}

Pulse	O_2 In	O_2 Out	CO Out	CO_2 Out	O_2 Taken Up
1(O_2)	36.0	0.0	0.0	20.7	15.3
2(O_2)	36.0	0.0	0.0	18.9	17.1
3(O_2)	36.0	0.0	0.0	14.8	21.2
4(O_2)	36.0	0.0	0.0	12.2	23.8
5(O_2)	36.0	0.0	0.0	10.2	25.8
6(O_2)	36.0	10.0	0.0	0.0	26.0
7(O_2)	36.0	17.6	0.0	0.0	18.4
8(O_2)	36.0	22.0	0.0	0.0	14.0
9(O_2)	36.0	26.1	0.0	0.0	9.9
10(O_2)	36.0	28.8	0.0	0.0	7.2

Total carbon burnt off catalyst as CO or CO_2 = 76.8 x 10^{17} atoms.

Table 5.24f Calculated Ratio of Isotopic Methanes Produced During the Interaction of 1:1 C_3H_4:C_3D_8 with a Chromia/K/alumina Catalyst at 400°C.

Pulse	CD_4	CD_3H	CD_2H_2	CDH_3	CH_4
1(C_3H_4/C_3D_8)	0	14	14	0	72
2(C_3H_4/C_3D_8)	0	11	11	11	67
3(C_3H_4/C_3D_8)	0	0	0	12	88
4(C_3H_4/C_3D_8)	6	0	0	12	82
5(C_3H_4/C_3D_8)	6	0	0	12	82
6(C_3H_4/C_3D_8)	0	0	17	0	83

Table 5.24g Normalised Mass Spectra for Unreacted Propane During the Interaction of 1:1 C_3H_4:C_3D_8 with a Chromia/K/alumina Catalyst at 400°C.

m/z	Pulse 1 (C_3H_4/C_3D_8)	Pulse 2 (C_3H_4/C_3D_8)	Pulse 3 (C_3H_4/C_3D_8)	Pulse 4 (C_3H_4/C_3D_8)	Pulse 5 (C_3H_4/C_3D_8)	Pulse 6 (C_3H_4/C_3D_8)
36	0.28	0.25	0.00	0.33	0.44	0.33
37	0.28	0.00	0.25	0.33	0.22	0.22
38	0.83	1.50	1.50	2.00	1.67	1.78
39	0.00	0.50	0.50	0.67	0.67	0.56
40	0.56	2.00	2.50	3.00	2.78	2.67
41	0.28	0.50	0.75	1.00	1.11	0.89
42	1.27	2.26	2.93	4.15	3.25	3.69
43	0.56	0.25	0.50	1.00	1.11	0.89
44	0.00	0.25	0.50	1.00	1.00	1.00
45	0.56	0.25	0.25	0.33	0.44	0.44
46	0.56	1.12	1.00	1.67	1.44	1.89
47	0.00	0.25	0.25	0.33	0.33	0.44
48	0.50	0.82	0.90	1.40	1.13	1.36
49	0.28	0.50	0.50	0.67	0.44	0.67
50	1.00	1.52	1.80	2.47	2.82	3.49
51	0.00	1.00	1.00	1.00	1.00	1.00
52	0.00	0.00	0.00	0.00	0.00	0.00

Experiment C(K)ADTH.02

Table 5.25a Product Distribution for the Interaction of Pulses of 1: 1 C_3H_4:C_3D_8 with a Chromia/K/alumina Catalyst at 500°C. (Catalyst weight = 0.1949 g; Pulse size = 36.0 x 10^{17} molecules).

Product molecules x 10^{17}

Pulse	CO	CX_4	CO_2	C_3X_6	C_3X_8
1(C_3H_4/C_3D_8)	3.2	24.5	0.4	trace	18.2
2(C_3H_4/C_3D_8)	8.4	28.6	1.8	trace	21.0
3(C_3H_4/C_3D_8)	6.7	20.8	1.1	trace	21.5
4(C_3H_4/C_3D_8)	7.1	24.3	0.5	trace	20.2
5(C_3H_4/C_3D_8)	6.5	18.5	1.5	trace	20.7
6(C_3H_4/C_3D_8)	4.5	13.6	1.6	trace	19.1

Table 5.25b Carbon Balance for the Interaction of Pulses of 1:1 C_3H_4:C_3D_8 with a Chromia/K/alumina Catalyst at 500°C. (Catalyst weight = 0.1949 g).

Carbon atoms x 10^{17}

Pulse	Carbon In	Carbon Out	Delta Carbon
1(C_3H_4/C_3D_8)	108.0	82.7	-25.3
2(C_3H_4/C_3D_8)	108.0	101.8	-6.2
3(C_3H_4/C_3D_8)	108.0	93.1	-14.9
4(C_3H_4/C_3D_8)	108.0	92.5	-15.5
5(C_3H_4/C_3D_8)	108.0	88.6	-19.4
6(C_3H_4/C_3D_8)	108.0	77.0	-31.0

Total carbon lost to the catalyst = 112.3 x 10^{17} atoms.

Experiment C(K)ADTH.02

Figure 5.22a Product Distribution for the Interaction of Pulses of 1: 1 C_3H_4:C_3D_8 with a Chromia/K/alumina Catalyst at 500°C. (Catalyst weight = 0.1949 g; Pulse size = 36.0 x 10^{17} molecules).

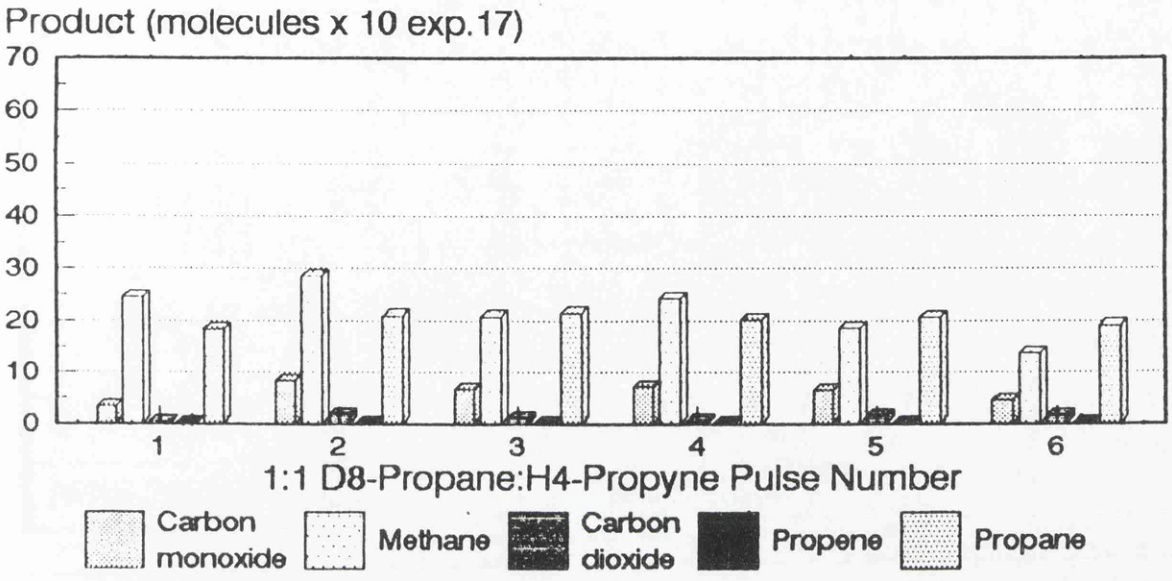


Figure 5.22b Carbon Balance for the Interaction of Pulses of 1:1 C_3H_4:C_3D_8 with a Chromia/K/alumina Catalyst at 500°C. (Catalyst weight = 0.1949 g).

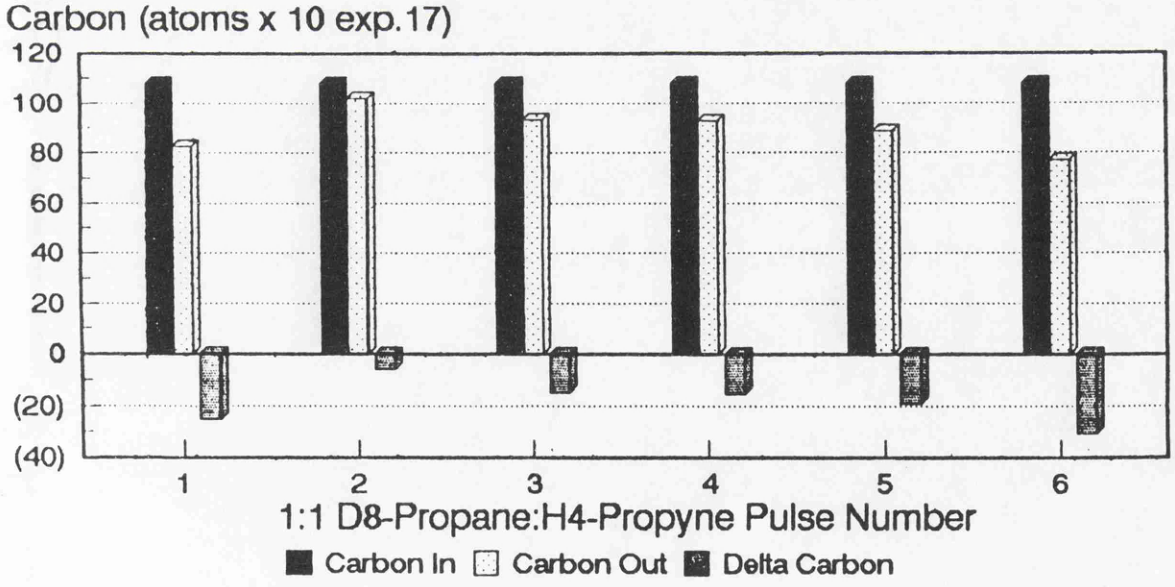


Table 5.25c Hydrogen Balance for the Interaction of Pulses of 1:1 C_3H_4:C_3D_8 with a Chromia/K/alumina Catalyst at 500°C. (Catalyst weight = 0.1949 g).

Hydrogen atoms x 10^{17}

Pulse	Hydrogen In	Hydrogen Out	Delta Hydrogen
1(C_3H_4/C_3D_8)	216.0	243.6	27.6
2(C_3H_4/C_3D_8)	216.0	282.4	66.4
3(C_3H_4/C_3D_8)	216.0	255.2	39.2
4(C_3H_4/C_3D_8)	216.0	258.8	42.8
5(C_3H_4/C_3D_8)	216.0	239.6	23.6
6(C_3H_4/C_3D_8)	216.0	207.2	-8.8

Total hydrogen gained from the catalyst = 190.8 x 10^{17} atoms.

Table 5.25d Ratio of Carbon:Hydrogen Lost to the Catalyst During the Interaction of Pulses of 1:1 C_3H_4:C_3D_8 with a Chromia/K/alumina Catalyst at 500°C. (Catalyst weight = 0.1949 g).

Pulse	1	2	3	4	5	6	Total
Ratio of C:H Lost to Catalyst	∞[a]	∞[a]	∞[a]	∞[a]	∞[a]	1:4	∞[a]

[a] ∞ means that only carbon was lost to the catalyst.

Figure 5.22c Hydrogen Balance for the Interaction of Pulses of 1:1 C_3H_4:C_3D_8 with a Chromia/K/alumina Catalyst at 500°C. (Catalyst weight = 0.1949 g).

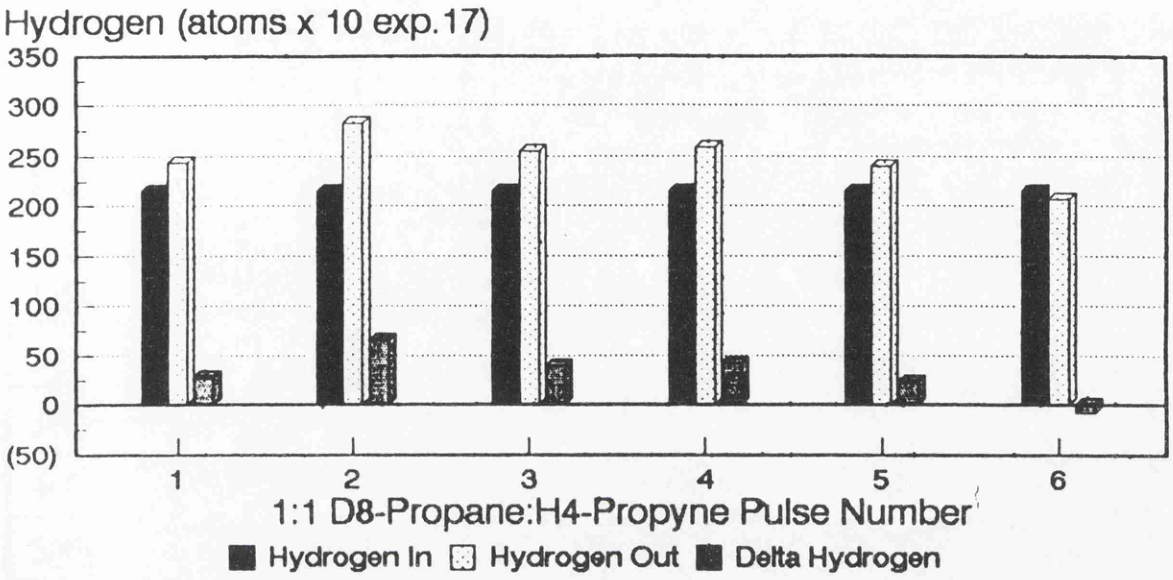


Table 5.25e Oxygen Balance for the Interaction of Dioxygen with the Used Chromia/K/alumina Catalyst at 500°C.
(Catalyst weight = 0.1949 g)

Molecules x 10^{17}

Pulse	O_2 In	O_2 Out	CO Out	CO_2 Out	O_2 Taken Up
1(O_2)	36.0	0.0	1.5	2.3	33.0
2(O_2)	36.0	0.0	1.1	1.2	34.2
3(O_2)	36.0	1.4	0.0	1.0	33.6
4(O_2)	36.0	1.4	0.0	0.4	34.2
5(O_2)	36.0	1.6	0.0	0.2	34.2
6(O_2)	36.0	2.1	0.0	0.0	33.9
7(O_2)	36.0	3.6	0.0	0.0	32.4
8(O_2)	36.0	7.3	0.0	0.0	28.7

Total carbon burnt off catalyst as CO or CO_2 = 7.7 x 10^{17} atoms.

Table 5.25f Calculated Ratio of Isotopic Methanes Produced During the Interaction of 1:1 C_3H_4:C_3D_8 with a Chromia/K/alumina Catalyst at 500°C.

Pulse	CD_4	CD_3H	CD_2H_2	CDH_3	CH_4
1(C_3H_4/C_3D_8)	0	0	3	0	97
2(C_3H_4/C_3D_8)	0	4	8	4	84
3(C_3H_4/C_3D_8)	0	4	11	4	81
4(C_3H_4/C_3D_8)	2	3	10	7	78
5(C_3H_4/C_3D_8)	2	4	11	7	76
6(C_3H_4/C_3D_8)	2	4	11	8	75

Table 5.25g Normalised Mass Spectra for Propene Produced During the Interaction of 1:1 C_3H_4:C_3D_8 with a Chromia/K/alumina Catalyst at 500°C.

m/z	Pulse 1 (C_3H_4/C_3D_8)	Pulse 2 (C_3H_4/C_3D_8)	Pulse 3 (C_3H_4/C_3D_8)	Pulse 4 (C_3H_4/C_3D_8)	Pulse 5 (C_3H_4/C_3D_8)	Pulse 6 (C_3H_4/C_3D_8)
36	0.04	0.05	0.06	0.03	0.07	0.04
37	0.14	0.16	0.18	0.13	0.15	0.15
38	0.23	0.24	0.26	0.26	0.22	0.23
39	0.81	0.84	0.88	0.81	0.81	0.77
40	0.35	0.42	0.50	0.52	0.48	0.46
41	1.00	1.00	1.00	1.00	1.00	1.00
42	0.86	0.87	1.03	1.06	1.04	1.08
43	0.19	0.26	0.35	0.39	0.41	0.50
44	0.02	0.05	0.00	0.00	0.00	0.00
45	0.05	0.05	0.06	0.06	0.07	0.04
46	0.09	0.13	0.18	0.13	0.07	0.08
47	0.00	0.03	0.03	0.00	0.00	0.00
48	0.05	0.05	0.06	0.03	0.04	0.04
49	0.02	0.05	0.06	0.03	0.04	0.04
50	0.14	0.13	0.32	0.26	0.11	0.15
51	0.04	0.05	0.09	0.06	0.04	0.08
52	0.19	0.18	0.35	0.26	0.22	0.15

Table 5.25h Normalised Mass Spectra for Unreacted Propane During the Interaction of 1:1 C_3H_4:C_3D_8 with a Chromia/K/alumina Catalyst at 500°C.

m/z	Pulse 1 (C_3H_4/C_3D_8)	Pulse 2 (C_3H_4/C_3D_8)	Pulse 3 (C_3H_4/C_3D_8)	Pulse 4 (C_3H_4/C_3D_8)	Pulse 5 (C_3H_4/C_3D_8)	Pulse 6 (C_3H_4/C_3D_8)
36	0.11	0.11	0.12	0.06	0.07	0.15
37	0.11	0.11	0.12	0.12	0.14	0.15
38	0.56	0.61	0.75	0.62	0.71	0.77
39	0.72	0.67	0.88	0.62	0.71	0.77
40	0.94	1.06	1.19	1.19	1.21	1.15
41	1.11	0.72	1.25	1.00	1.21	1.23
42	1.70	1.73	1.94	1.93	2.17	2.22
43	0.22	0.33	0.38	0.38	0.43	0.54
44	0.17	0.67	0.12	0.00	0.00	0.08
45	0.50	0.44	0.50	0.50	0.43	0.46
46	0.56	0.75	0.69	0.66	0.79	0.85
47	0.22	0.22	0.25	0.25	0.21	0.23
48	0.47	0.46	0.49	0.51	0.44	0.50
49	0.89	0.89	0.88	0.88	0.86	0.92
50	0.88	0.89	1.10	1.04	1.24	1.25
51	1.00	1.00	1.00	1.00	1.00	1.00
52	0.00	0.00	0.00	0.00	0.00	0.00

Experiment C(K)ADTH.03

Table 5.26a Product Distribution for the Interaction of Pulses of 1: 1 C_3H_4:C_3D_8 with a Chromia/K/alumina Catalyst at 550°C. (Catalyst weight = 0.1945 g; Pulse size = 36.0 x 10^{17} molecules).

Product molecules x 10^{17}

Pulse	CO	CX_4	CO_2	C_3X_6	C_3X_8
1(C_3H_4/C_3D_8)	10.2	22.7	14.5	4.4	4.3
2(C_3H_4/C_3D_8)	10.0	27.7	4.0	7.7	7.4
3(C_3H_4/C_3D_8)	11.7	27.8	3.1	8.3	7.1
4(C_3H_4/C_3D_8)	9.6	23.0	0.5	9.4	7.0
5(C_3H_4/C_3D_8)	11.6	26.6	3.7	8.9	6.5
6(C_3H_4/C_3D_8)	12.1	33.5	3.5	9.3	6.9

Table 5.26b Carbon Balance for the Interaction of Pulses of 1:1 C_3H_4:C_3D_8 with a Chromia/K/alumina Catalyst at 550°C. (Catalyst weight = 0.1945 g).

Carbon atoms x 10^{17}

Pulse	Carbon In	Carbon Out	Delta Carbon
1(C_3H_4/C_3D_8)	108.0	73.5	-34.5
2(C_3H_4/C_3D_8)	108.0	87.0	-21.0
3(C_3H_4/C_3D_8)	108.0	88.8	-19.2
4(C_3H_4/C_3D_8)	108.0	82.3	-25.7
5(C_3H_4/C_3D_8)	108.0	88.1	-19.9
6(C_3H_4/C_3D_8)	108.0	97.7	-10.3

Total carbon lost to the catalyst = 130.6 x 10^{17} atoms.

Experiment C(K)ADTH.03

Figure 5.23a Product Distribution for the Interaction of Pulses of 1: 1 C_3H_4:C_3D_8 with a Chromia/K/alumina Catalyst at 550°C. (Catalyst weight = 0.1945 g; Pulse size = 36.0 x 10^{17} molecules).

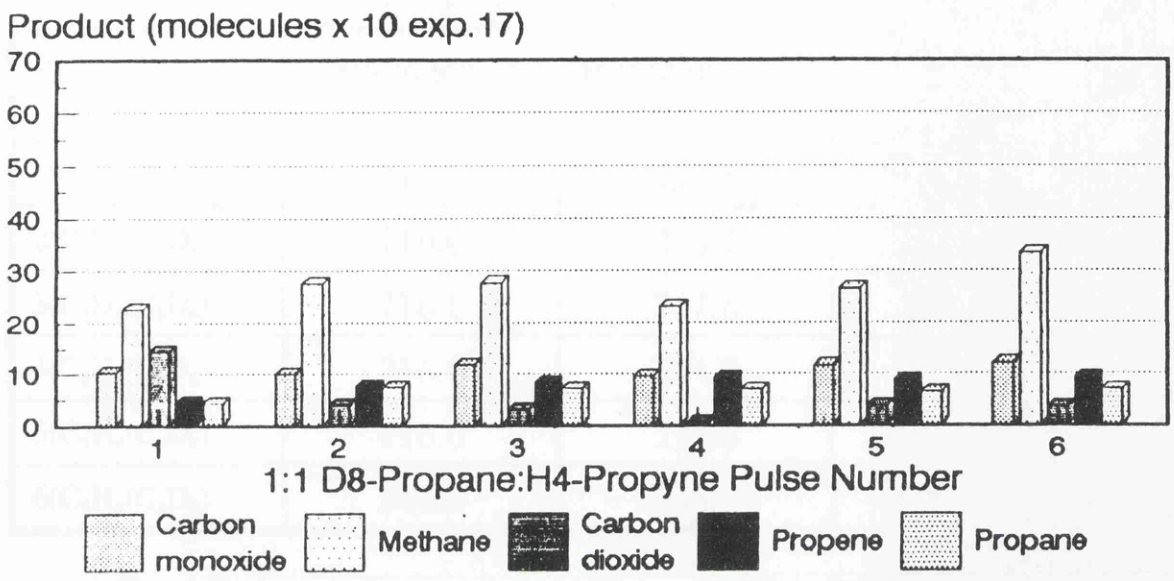


Figure 5.23b Carbon Balance for the Interaction of Pulses of 1:1 C_3H_4:C_3D_8 with a Chromia/K/alumina Catalyst at 550°C. (Catalyst weight = 0.1945 g).

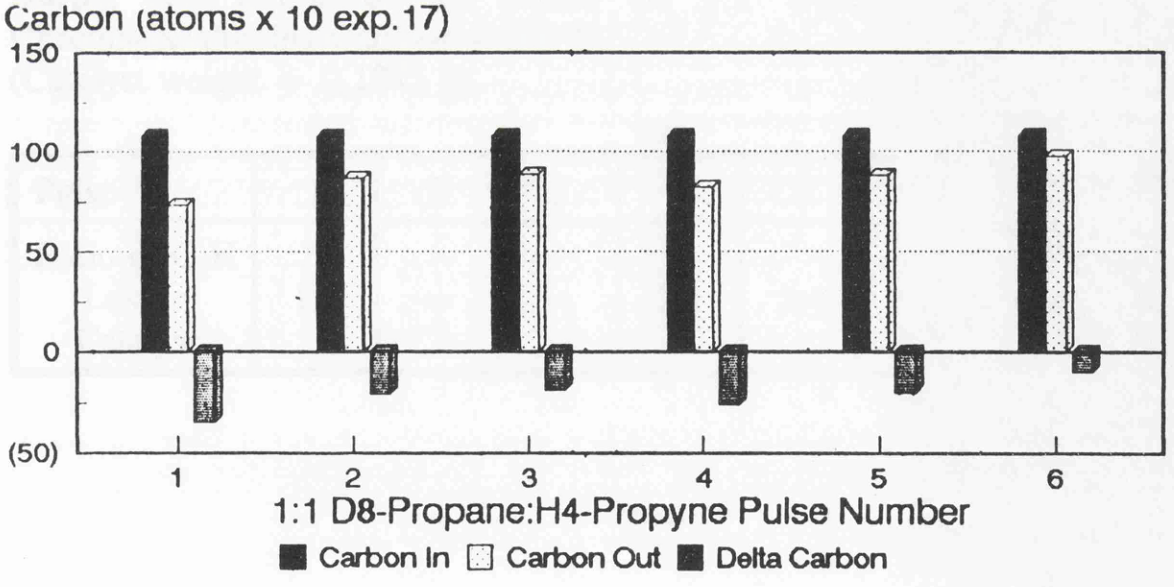


Table 5.26c Hydrogen Balance for the Interaction of Pulses of 1:1 C_3H_4:C_3D_8 with a Chromia/K/alumina Catalyst at 550°C. (Catalyst weight = 0.1945 g).

Hydrogen atoms x 10^{17}

Pulse	Hydrogen In	Hydrogen Out	Delta Hydrogen
1(C_3H_4/C_3D_8)	216.0	151.6	-64.4
2(C_3H_4/C_3D_8)	216.0	216.2	0.2
3(C_3H_4/C_3D_8)	216.0	217.8	1.8
4(C_3H_4/C_3D_8)	216.0	204.4	-11.6
5(C_3H_4/C_3D_8)	216.0	211.8	-4.2
6(C_3H_4/C_3D_8)	216.0	245.0	29.0

Total hydrogen lost to the catalyst = 49.2 x 10^{17} atoms.

Table 5.26d Ratio of Carbon:Hydrogen Lost to the Catalyst During the Interaction of Pulses of 1:1 C_3H_4:C_3D_8 with a Chromia/K/alumina Catalyst at 550°C. (Catalyst weight = 0.1945 g).

Pulse	1	2	3	4	5	6	Total
Ratio of C:H Lost to Catalyst	1:2	∞	∞	2:1	5:1	∞	1:3

Figure 5.23c Hydrogen Balance for the Interaction of Pulses of 1:1 C_3H_4:C_3D_8 with a Chromia/K/alumina Catalyst at 550°C. (Catalyst weight = 0.1945 g).

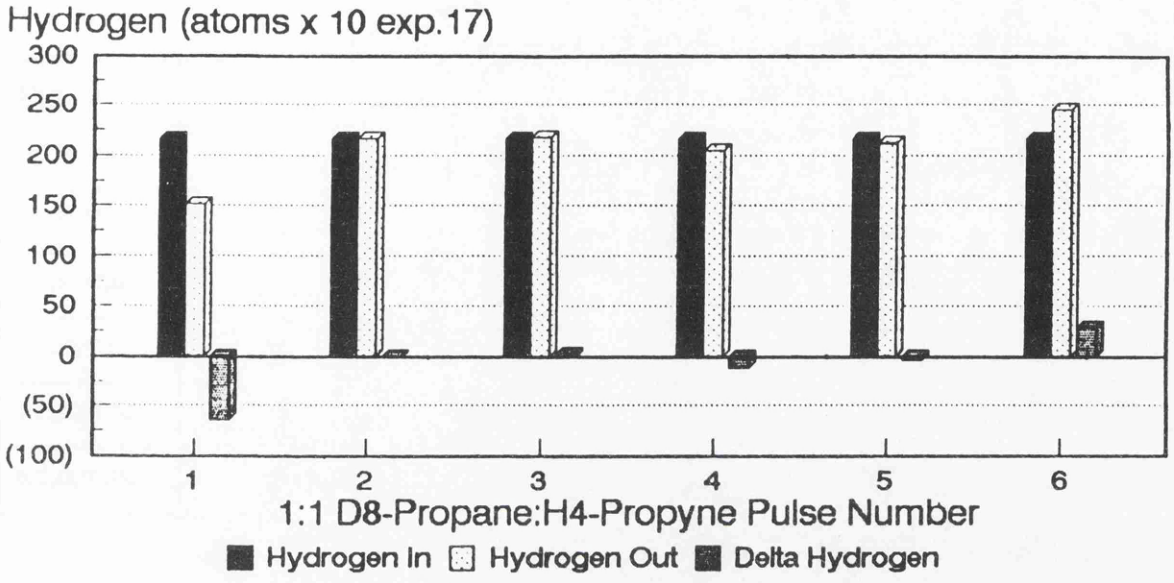


Table 5.26e Calculated ratio of Isotopic Methanes Produced During the Interaction of 1:1 C_3H_4:C_3D_8 with a Chromia/K/alumina Catalyst at 550°C.

Pulse	CD_4	CD_3H	CD_2H_2	CDH_3	CH_4
1(C_3H_4/C_3D_8)	0	0	8	8	84
2(C_3H_4/C_3D_8)	0	3	14	10	73
3(C_3H_4/C_3D_8)	0	4	11	19	66
4(C_3H_4/C_3D_8)	0	4	16	20	60
5(C_3H_4/C_3D_8)	0	4	15	23	58
6(C_3H_4/C_3D_8)	0	3	17	28	52

Table 5.26f Normalised Mass Spectra for Propene Produced During the Interaction of 1:1 C_3H_4:C_3D_8 with a Chromia/K/alumina Catalyst at 550°C.

m/z	Pulse 1 (C_3H_4/C_3D_8)	Pulse 2 (C_3H_4/C_3D_8)	Pulse 3 (C_3H_4/C_3D_8)	Pulse 4 (C_3H_4/C_3D_8)	Pulse 5 (C_3H_4/C_3D_8)	Pulse 6 (C_3H_4/C_3D_8)
36	0.04	0.03	0.04	0.04	0.04	0.04
37	0.16	0.17	0.19	0.19	0.21	0.21
38	0.28	0.27	0.30	0.31	0.33	0.33
39	0.88	0.83	0.89	0.88	0.88	0.92
40	0.48	0.53	0.59	0.69	0.79	0.83
41	1.00	1.00	1.00	1.00	1.00	1.00
42	0.96	1.00	1.15	1.23	1.29	1.33
43	0.20	0.40	0.52	0.58	0.71	0.83
44	0.00	0.07	0.04	0.08	0.12	0.21
45	0.00	0.03	0.11	0.04	0.08	0.17
46	0.12	0.07	0.15	0.15	0.21	0.21
47	0.04	0.03	0.04	0.12	0.08	0.08
48	0.08	0.07	0.07	0.08	0.12	0.17
49	0.12	0.07	0.07	0.15	0.17	0.12
50	0.24	0.13	0.22	0.31	0.29	0.33
51	0.16	0.13	0.15	0.19	0.17	0.21
52	0.24	0.20	0.26	0.31	0.33	0.33

Table 5.26g Normalised Mass Spectra for Unreacted Propane During the Interaction of 1:1 C_3H_4:C_3D_8 with a Chromia/K/alumina Catalyst at 550°C.

m/z	Pulse 1 (C_3H_4/C_3D_8)	Pulse 2 (C_3H_4/C_3D_8)	Pulse 3 (C_3H_4/C_3D_8)	Pulse 4 (C_3H_4/C_3D_8)	Pulse 5 (C_3H_4/C_3D_8)	Pulse 6 (C_3H_4/C_3D_8)
36	0.14	0.12	0.12	0.12	0.12	0.12
37	0.29	0.38	0.25	0.25	0.25	0.25
38	0.71	0.75	0.75	0.75	0.75	0.75
39	1.43	1.62	1.38	1.12	1.00	1.25
40	1.14	1.50	1.25	1.25	1.38	1.50
41	1.71	2.00	1.62	1.50	1.50	1.50
42	1.83	2.20	1.94	1.94	2.07	1.92
43	0.43	0.75	0.75	0.62	0.75	1.00
44	0.00	0.25	0.00	0.00	0.12	0.12
45	0.29	0.38	0.50	0.25	0.38	0.62
46	0.43	0.38	0.38	0.50	0.50	0.38
47	0.29	0.25	0.38	0.38	0.38	0.50
48	0.57	0.48	0.48	0.48	0.48	0.58
49	0.86	0.88	0.88	0.88	0.88	0.88
50	0.71	0.70	0.58	0.70	0.7	0.65
51	1.00	1.00	1.00	1.00	1.00	1.00
52	0.00	0.00	0.00	0.00	0.00	0.00

Experiment C(K)ADTH.04

Table 5.27a Product Distribution for the Interaction of Pulses of 1: 1 C_3H_4:C_3D_8 with a Chromia/K/alumina Catalyst at 600°C. (Catalyst weight = 0.2226 g; Pulse size = 36.0 x 10^{17} molecules).

Product molecules x 10^{17}

Pulse	CO	CX_4	CO_2	C_3X_6	C_3X_8
1(C_3H_4/C_3D_8)	8.6	8.9	69.1	0.0	0.0
2(C_3H_4/C_3D_8)	14.8	23.0	41.5	0.0	0.0
3(C_3H_4/C_3D_8)	20.2	29.9	7.6	6.7	0.8
4(C_3H_4/C_3D_8)	20.2	25.3	6.4	6.8	1.1
5(C_3H_4/C_3D_8)	18.1	23.2	5.4	6.1	1.2
6(C_3H_4/C_3D_8)	16.6	19.4	4.7	6.5	0.3

Table 5.27b Carbon Balance for the Interaction of Pulses of 1:1 C_3H_4:C_3D_8 with a Chromia/K/alumina Catalyst at 600°C. (Catalyst weight = 0.2226 g).

Carbon atoms x 10^{17}

Pulse	Carbon In	Carbon Out	Delta Carbon
1(C_3H_4/C_3D_8)	108.0	86.6	-21.4
2(C_3H_4/C_3D_8)	108.0	79.3	-28.7
3(C_3H_4/C_3D_8)	108.0	80.2	-27.8
4(C_3H_4/C_3D_8)	108.0	75.6	-32.4
5(C_3H_4/C_3D_8)	108.0	68.6	-39.4
6(C_3H_4/C_3D_8)	108.0	61.1	-46.9

Total carbon lost to the catalyst = 196.6 x 10^{17} atoms.

Experiment C(K)ADTH.04

Figure 5.24a Product Distribution for the Interaction of Pulses of 1: 1 C_3H_4:C_3D_8 with a Chromia/K/alumina Catalyst at 600°C. (Catalyst weight = 0.2226 g; Pulse size = 36.0 x 10^{17} molecules).

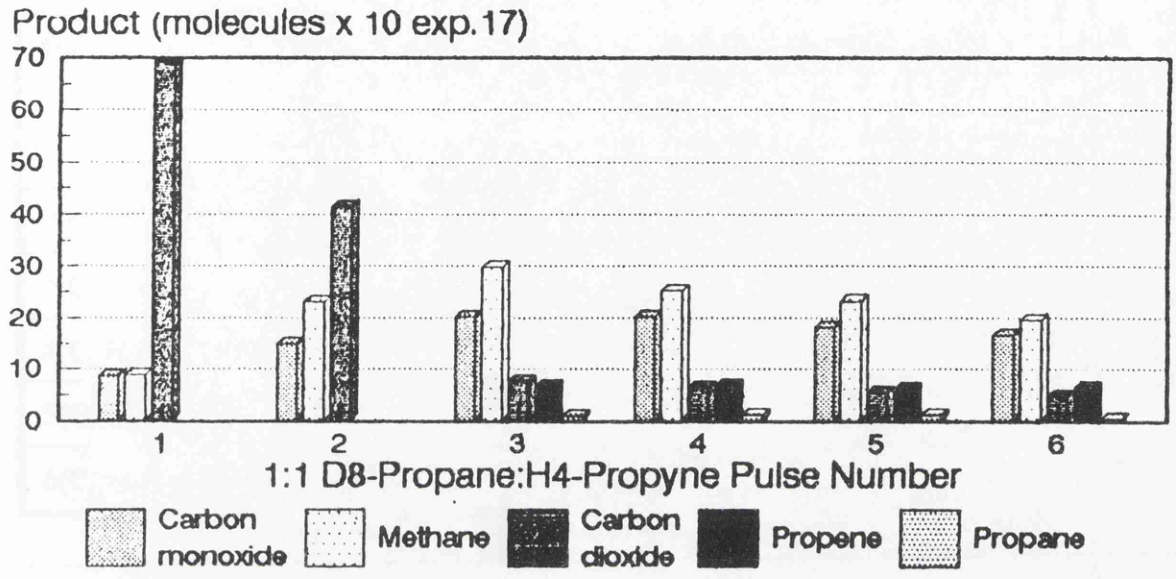


Figure 5.24b Carbon Balance for the Interaction of Pulses of 1:1 C_3H_4:C_3D_8 with a Chromia/K/alumina Catalyst at 600°C. (Catalyst weight = 0.2226 g).

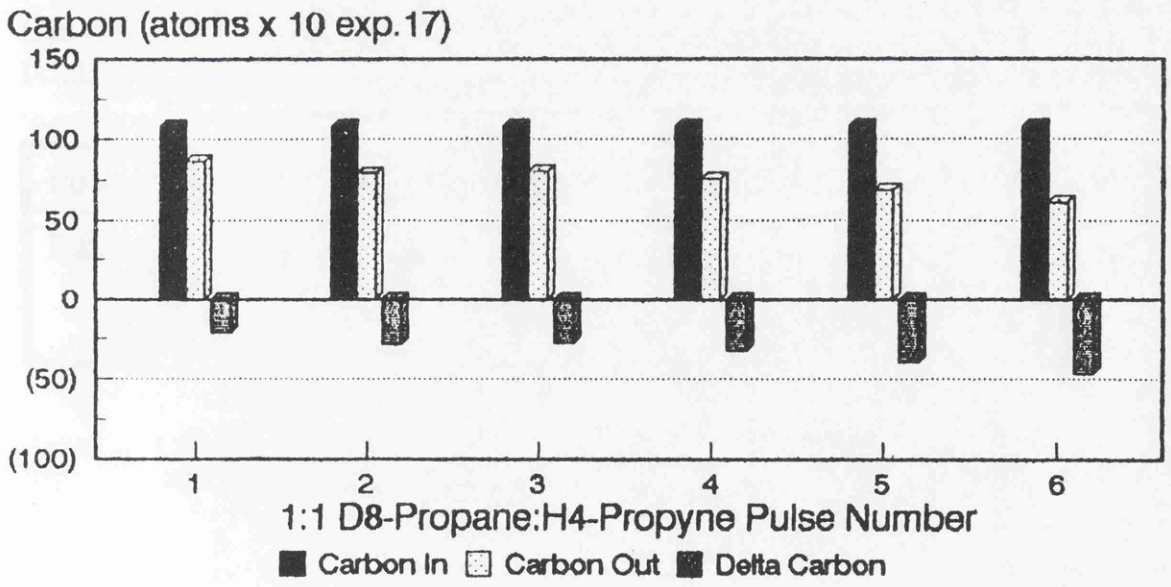


Table 5.27c Hydrogen Balance for the Interaction of Pulses of 1:1 C_3H_4:C_3D_8 with a Chromia/K/alumina Catalyst at 600°C. (Catalyst weight = 0.2226 g).

Hydrogen atoms x 10^{17}

Pulse	Hydrogen In	Hydrogen Out	Delta Hydrogen
1(C_3H_4/C_3D_8)	216.0	35.6	-180.4
2(C_3H_4/C_3D_8)	216.0	92.0	-124.0
3(C_3H_4/C_3D_8)	216.0	166.2	-49.8
4(C_3H_4/C_3D_8)	216.0	150.8	-65.2
5(C_3H_4/C_3D_8)	216.0	139.0	-77.0
6(C_3H_4/C_3D_8)	216.0	119.0	-97.0

Total hydrogen lost to the catalyst = 693.4 x 10^{17} atoms.

Table 5.27d Ratio of Carbon:Hydrogen Lost to the Catalyst During the Interaction of Pulses of 1:1 C_3H_4:C_3D_8 with a Chromia/K/alumina Catalyst at 600°C. (Catalyst weight = 0.2226 g).

Pulse	1	2	3	4	5	6	Total
Ratio of C:H Lost to Catalyst	1:8	1:4	1:2	1:2	1:2	1:2	1:4

Figure 5.24c Hydrogen Balance for the Interaction of Pulses of 1:1 C_3H_4:C_3D_8 with a Chromia/K/alumina Catalyst at 600°C. (Catalyst weight = 0.2226 g).

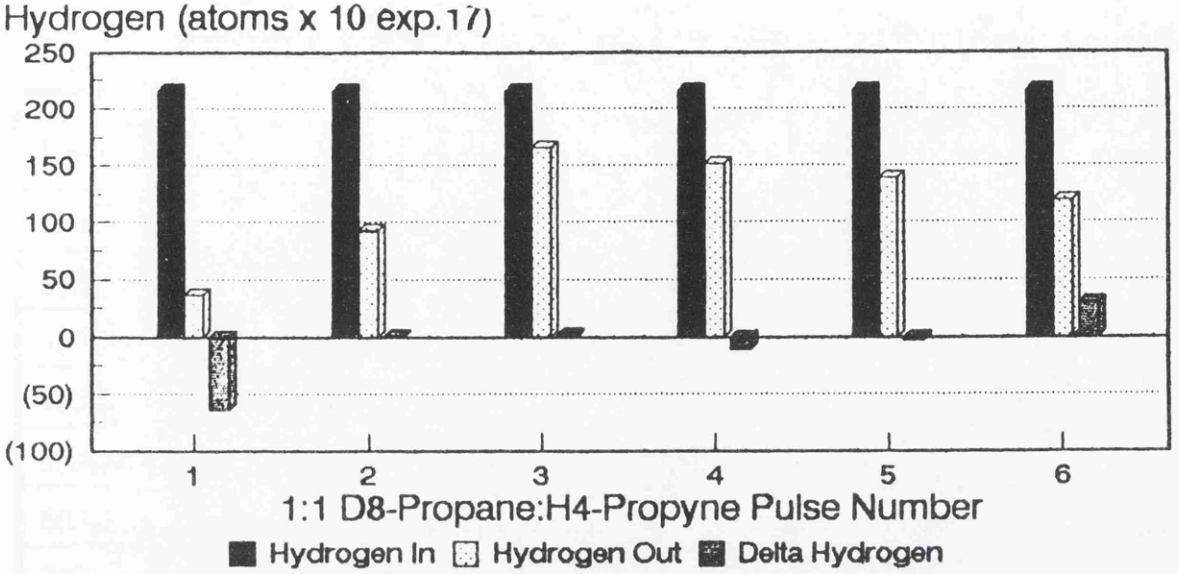


Table 5.27e Oxygen Balance for the Interaction of Dioxygen with the Used Chromia/K/alumina Catalyst at 600°C.
(Catalyst weight = 0.2226 g)

Molecules x 10^{17}

Pulse	O_2 In	O_2 Out	CO Out	CO_2 Out	O_2 Taken Up
1(O_2)	36.0	0.0	1.3	1.4	34.0
2(O_2)	36.0	0.0	1.4	0.9	34.4
3(O_2)	36.0	1.7	0.0	1.2	33.1
4(O_2)	36.0	2.0	0.0	1.1	32.9
5(O_2)	36.0	1.2	0.0	0.7	34.1
6(O_2)	36.0	2.7	0.0	0.0	33.3
7(O_2)	36.0	1.8	0.0	0.0	34.2
8(O_2)	36.0	6.6	0.0	0.0	29.4
9(O_2)	36.0	13.2	0.0	0.0	22.8
10(O_2)	36.0	15.4	0.0	0.0	20.6
11(O_2)	36.0	19.0	0.0	0.0	17.0
12(O_2)	36.0	19.2	0.0	0.0	16.8

Total carbon burnt off catalyst as CO or CO_2 = 8.0 x 10^{17} atoms.

Table 5.27f Calculated Ratio of Isotopic Methanes Produced During the Interaction of 1:1 C_3H_4:C_3D_8 with a Chromia/K/alumina Catalyst at 600°C.

Pulse	CD_4	CD_3H	CD_2H_2	CDH_3	CH_4
1(C_3H_4/C_3D_8)	0	0	17	0	83
2(C_3H_4/C_3D_8)	2	2	16	25	55
3(C_3H_4/C_3D_8)	2	5	25	30	38
4(C_3H_4/C_3D_8)	2	5	28	32	33
5(C_3H_4/C_3D_8)	2	8	29	32	29
6(C_3H_4/C_3D_8)	2	8	32	30	28

Table 5.27g Normalised Mass Spectra for Propene Produced During the Interaction of 1:1 C_3H_4:C_3D_8 with a Chromia/K/alumina Catalyst at 600°C.

m/z	Pulse 3 (C_3H_4/C_3D_8)	Pulse 4 (C_3H_4/C_3D_8)	Pulse 5 (C_3H_4/C_3D_8)	Pulse 6 (C_3H_4/C_3D_8)
36	0.05	0.05	0.05	0.06
37	0.21	0.18	0.21	0.17
38	0.32	0.32	0.32	0.33
39	0.95	0.79	0.79	0.78
40	1.03	0.92	1.03	1.00
41	1.00	1.00	1.00	1.00
42	1.26	1.26	1.32	1.28
43	1.03	1.08	1.18	1.22
44	0.42	0.50	0.55	0.64
45	0.13	0.18	0.32	0.33
46	0.05	0.08	0.11	0.11
47	0.00	0.03	0.03	0.03
48	0.00	0.03	0.03	0.03
49	0.00	0.03	0.03	0.03
50	0.03	0.05	0.05	0.06
51	0.00	0.05	0.00	0.03
52	0.03	0.05	0.08	0.06

Table 5.27h Normalised Mass Spectra for Unreacted Propane During the Interaction of 1:1 C_3H_4:C_3D_8 with a Chromia/K/alumina Catalyst at 600°C.

m/z	Pulse 3 (C_3H_4/C_3D_8)	Pulse 4 (C_3H_4/C_3D_8)	Pulse 5 (C_3H_4/C_3D_8)	Pulse 6 (C_3H_4/C_3D_8)
36	0.25	0.25	0.33	0.25
37	1.00	0.75	1.00	0.50
38	1.75	1.25	2.00	1.50
39	4.00	2.50	3.33	2.75
40	4.50	3.25	5.00	3.50
41	3.75	3.25	5.00	3.50
42	5.07	4.57	7.09	4.82
43	2.75	2.50	5.00	4.00
44	0.25	0.25	0.67	0.50
45	0.50	0.50	2.00	1.50
46	0.75	0.50	1.33	0.75
47	0.25	0.25	0.67	0.25
48	0.60	0.35	1.13	0.60
49	1.00	1.00	1.67	1.00
50	0.70	0.95	1.27	0.95
51	1.00	1.00	1.00	1.00
52	0.00	0.00	0.00	0.00

Experiment C(K)ATH.01

Table 5.28a Product Distribution for the Interaction of Pulses of 1: 1 C_3H_4:C_3H_8 with a Chromia/K/alumina Catalyst at 550°C. (Catalyst weight = 0.2048 g; Pulse size = 36.0 x 10^{17} molecules).

Product molecules x 10^{17}

Pulse	CO	CH_4	CO_2	C_3H_6	C_3H_8
1(C_3H_4/C_3H_8)	8.6	10.6	46.3	0.0	0.0
2(C_3H_4/C_3H_8)	10.4	13.3	48.8	0.0	0.0
3(C_3H_4/C_3H_8)	8.7	25.8	36.3	0.0	0.0
4(C_3H_4/C_3H_8)	13.6	32.7	4.7	7.4	6.0
5(C_3H_4/C_3H_8)	12.6	36.5	3.8	8.0	7.2
6(C_3H_4/C_3H_8)	8.1	45.2	4.7	8.3	8.0

Table 5.28b Carbon Balance for the Interaction of Pulses of 1:1 C_3H_4:C_3H_8 with a Chromia/K/alumina Catalyst at 550°C. (Catalyst weight = 0.2048 g).

Carbon atoms x 10^{17}

Pulse	Carbon In	Carbon Out	Delta Carbon
1(C_3H_4/C_3H_8)	108.0	65.5	-42.5
2(C_3H_4/C_3H_8)	108.0	72.5	-35.5
3(C_3H_4/C_3H_8)	108.0	70.8	-37.2
4(C_3H_4/C_3H_8)	108.0	91.2	-16.8
5(C_3H_4/C_3H_8)	108.0	98.5	-9.5
6(C_3H_4/C_3H_8)	108.0	106.9	-1.1

Total carbon lost to the catalyst = 142.6 x 10^{17} atoms.

Experiment C(K)ATH.01

Figure 5.25a Product Distribution for the Interaction of Pulses of 1: 1 C_3H_4:C_3H_8 with a Chromia/K/alumina Catalyst at 550°C. (Catalyst weight = 0.2048 g; Pulse size = 36.0 x 10^{17} molecules).

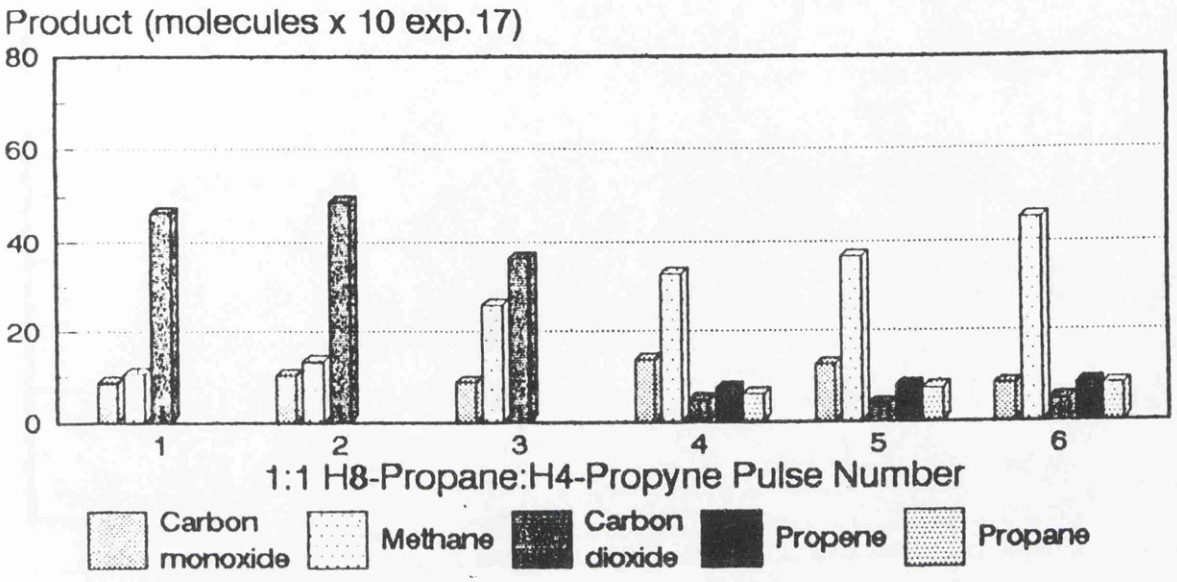


Figure 5.25b Carbon Balance for the Interaction of Pulses of 1:1 C_3H_4:C_3H_8 with a Chromia/K/alumina Catalyst at 550°C. (Catalyst weight = 0.2048 g).

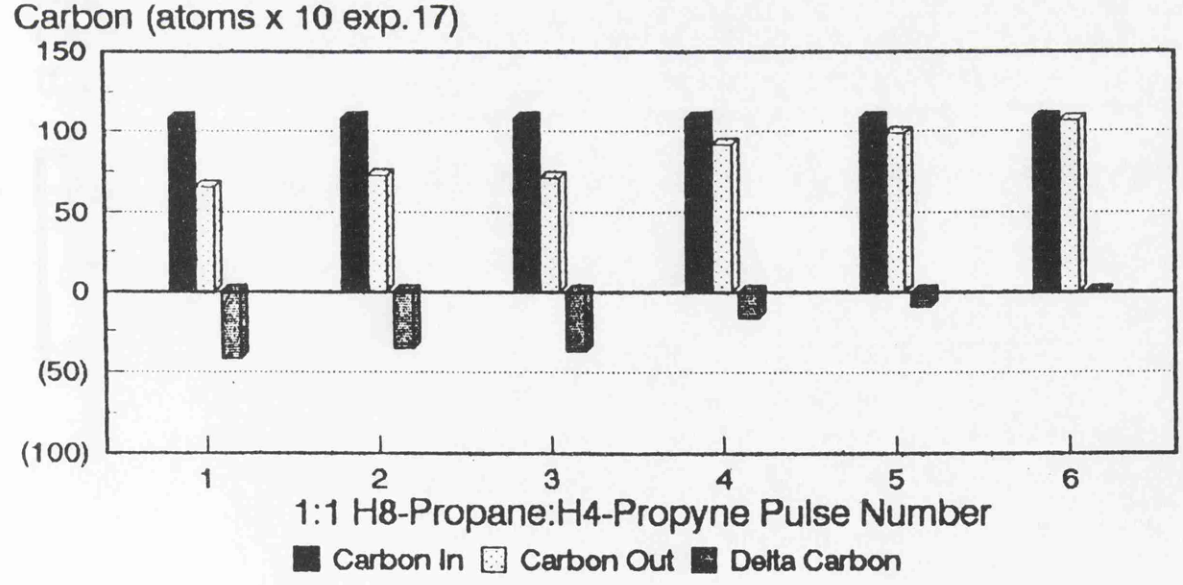


Table 5.28c Hydrogen Balance for the Interaction of Pulses of 1:1 C_3H_4:C_3H_8 with a Chromia/K/alumina Catalyst at 550°C. (Catalyst weight = 0.2048 g).

Hydrogen atoms x 10^{17}

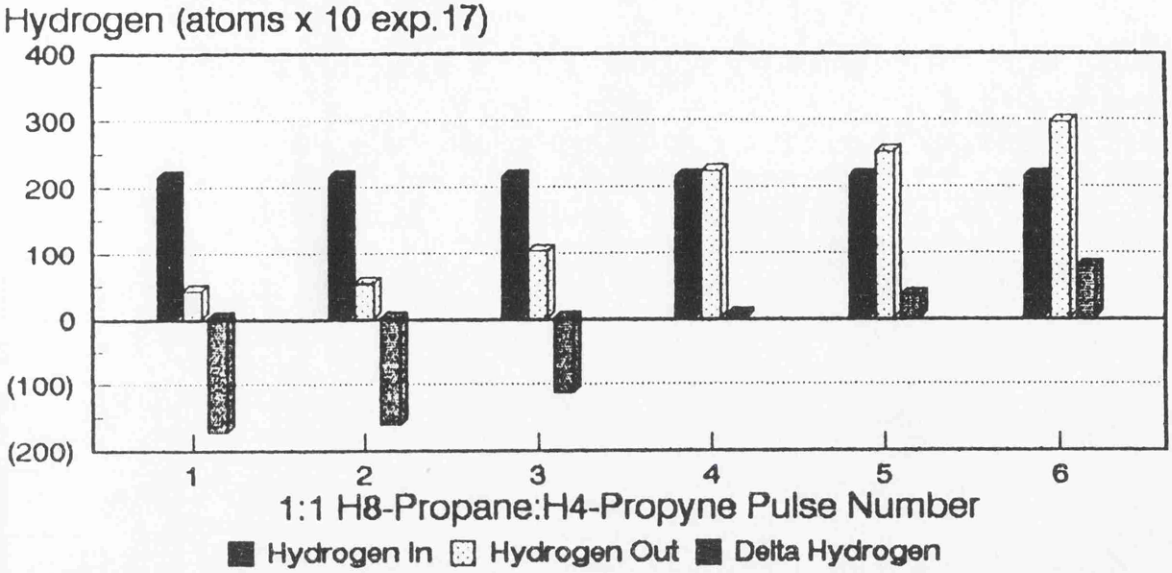
Pulse	Hydrogen In	Hydrogen Out	Delta Hydrogen
1(C_3H_4/C_3H_8)	216.0	42.4	-173.6
2(C_3H_4/C_3H_8)	216.0	53.2	-162.8
3(C_3H_4/C_3H_8)	216.0	103.2	-112.8
4(C_3H_4/C_3H_8)	216.0	223.2	7.2
5(C_3H_4/C_3H_8)	216.0	251.6	35.6
6(C_3H_4/C_3H_8)	216.0	294.6	78.6

Total hydrogen lost to the catalyst = 327.8 x 10^{17} atoms.

Table 5.28d Ratio of Carbon:Hydrogen Lost to the Catalyst During the Interaction of Pulses of 1:1 C_3H_4:C_3H_8 with a Chromia/K/alumina Catalyst at 550°C. (Catalyst weight = 0.2048 g).

Pulse	1	2	3	4	5	6	Total
Ratio of C:H Lost to Catalyst	1:4	1:5	1:3	∞	∞	∞	1:2

Figure 5.25c Hydrogen Balance for the Interaction of Pulses of 1:1 C_3H_4:C_3H_8 with a Chromia/K/alumina Catalyst at 550°C. (Catalyst weight = 0.2048 g).



Experiment C(K)ATH.02

Table 5.29a Product Distribution for the Interaction of Pulses of 1: 1 C_3H_4:C_3H_8 with a Chromia/K/alumina Catalyst at 550°C. (Catalyst weight = 0.2149 g; Pulse size = 72.0 x 10^{17} molecules).

Product molecules x 10^{17}

Pulse	CO	CH_4	CO_2	C_3H_6	C_3H_8
1(C_3H_4/C_3H_8)	26.6	33.6	77.9	7.7	8.0
2(C_3H_4/C_3H_8)	16.4	37.0	4.2	12.4	17.7
3(C_3H_4/C_3H_8)	23.8	52.0	3.2	13.3	21.0
4(C_3H_4/C_3H_8)	8.7	20.5	1.5	7.8	11.2
5(C_3H_4/C_3H_8)	14.8	33.9	0.8	13.5	21.3
6(C_3H_4/C_3H_8)	22.3	48.8	1.2	13.6	22.6

Table 5.29b Carbon Balance for the Interaction of Pulses of 1:1 C_3H_4:C_3H_8 with a Chromia/K/alumina Catalyst at 550°C. (Catalyst weight = 0.2149 g).

Carbon atoms x 10^{17}

Pulse	Carbon In	Carbon Out	Delta Carbon
1(C_3H_4/C_3H_8)	216.0	185.2	-30.8
2(C_3H_4/C_3H_8)	216.0	147.9	-68.1
3(C_3H_4/C_3H_8)	216.0	181.9	-34.1
4(C_3H_4/C_3H_8)	216.0	87.7	-128.3
5(C_3H_4/C_3H_8)	216.0	153.9	-62.1
6(C_3H_4/C_3H_8)	216.0	180.9	-35.1

Total carbon lost to the catalyst = 358.5 x 10^{17} atoms.

Experiment C(K)ATH.02

Figure 5.26a Product Distribution for the Interaction of Pulses of 1: 1 C_3H_4:C_3H_8 with a Chromia/K/alumina Catalyst at 550°C. (Catalyst weight = 0.2149 g; Pulse size = 72.0 x 10^{17} molecules).

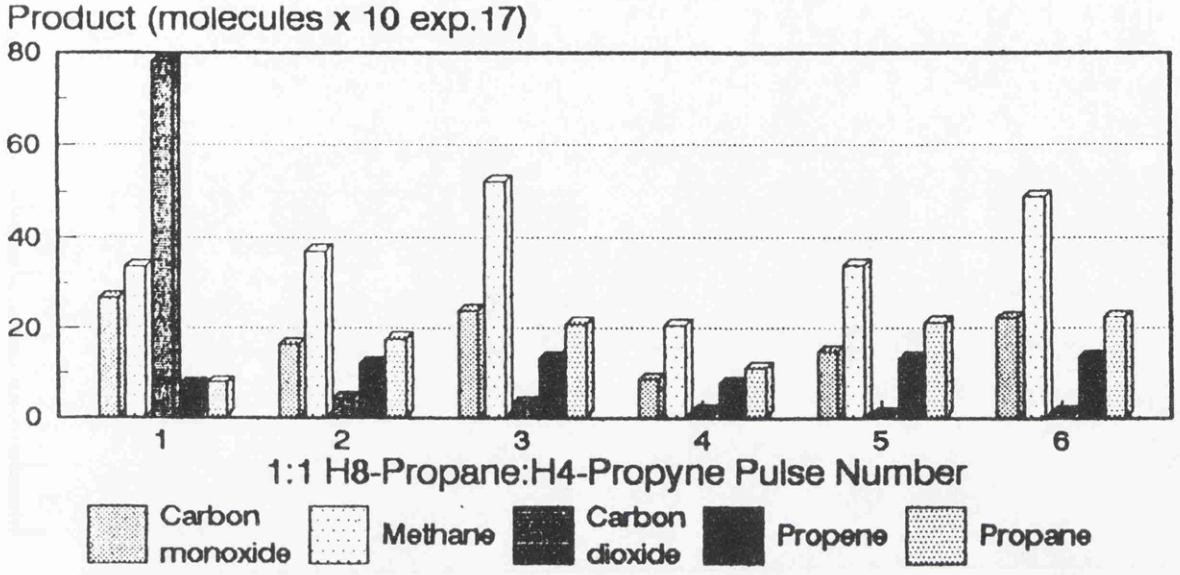


Figure 5.26b Carbon Balance for the Interaction of Pulses of 1:1 C_3H_4:C_3H_8 with a Chromia/K/alumina Catalyst at 550°C. (Catalyst weight = 0.2149 g).

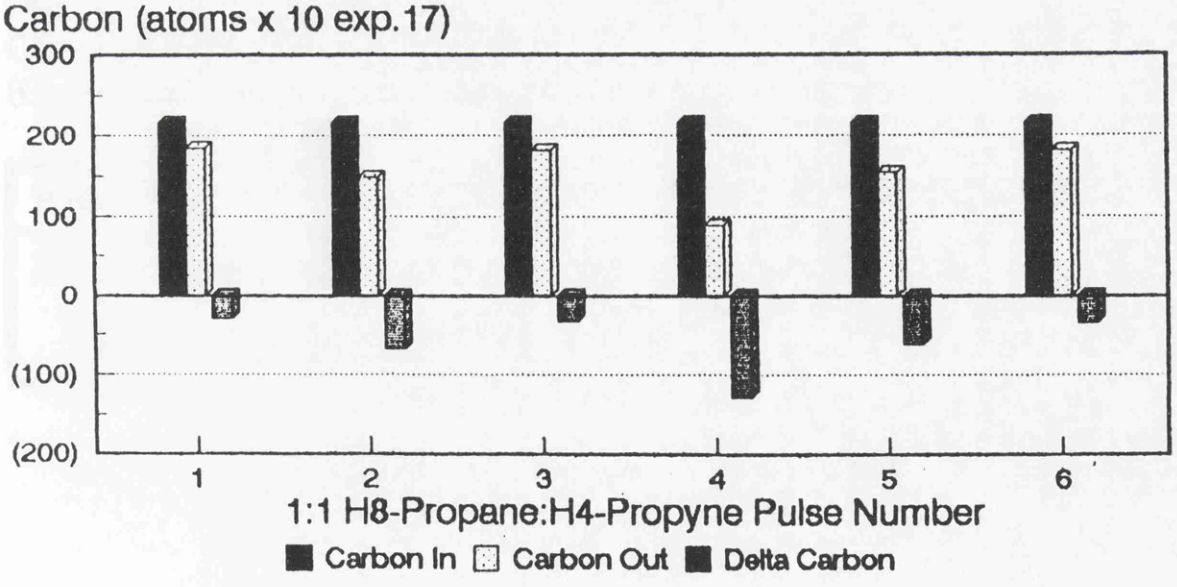


Table 5.29c Hydrogen Balance for the Interaction of Pulses of 1:1 C_3H_4:C_3H_8 with a Chromia/K/alumina Catalyst at 550°C. (Catalyst weight = 0.2149 g).

Hydrogen atoms x 10^{17}

Pulse	Hydrogen In	Hydrogen Out	Delta Hydrogen
1(C_3H_4/C_3D_8)	432.0	244.6	-187.4
2(C_3H_4/C_3D_8)	432.0	364.0	-68.0
3(C_3H_4/C_3D_8)	432.0	455.8	23.8
4(C_3H_4/C_3D_8)	432.0	218.4	-213.6
5(C_3H_4/C_3D_8)	432.0	387.0	-45.0
6(C_3H_4/C_3D_8)	432.0	457.6	25.6

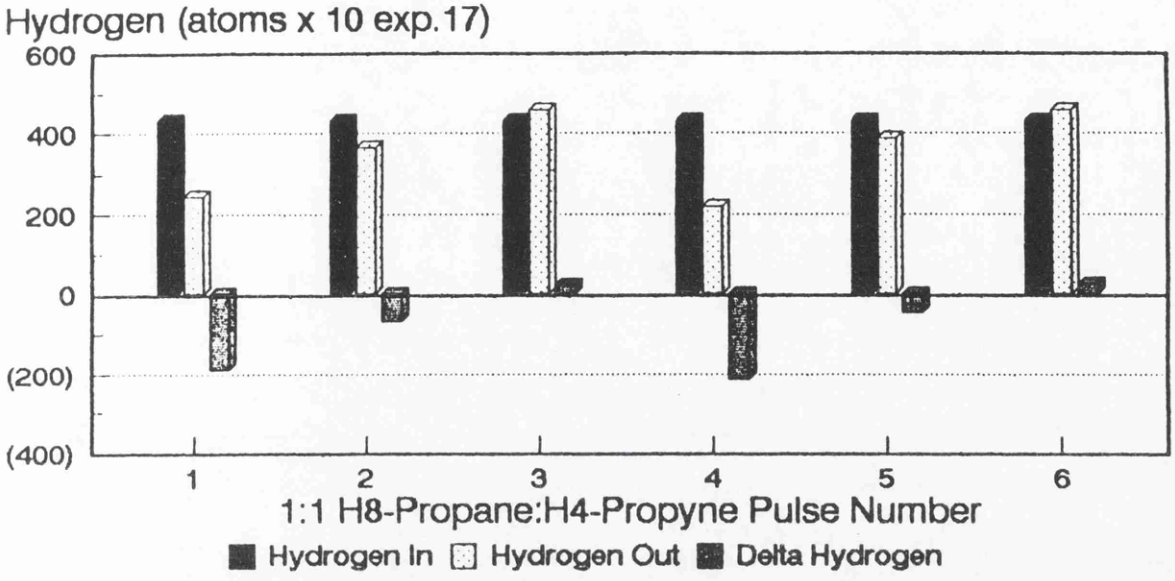
Total hydrogen lost to the catalyst = 464.6 x 10^{17} atoms.

Table 5.29d Ratio of Carbon:Hydrogen Lost to the Catalyst During the Interaction of Pulses of 1:1 C_3H_4:C_3H_8 with a Chromia/K/alumina Catalyst at 550°C. (Catalyst weight = 0.2149 g).

Pulse	1	2	3	4	5	6	Total
Ratio of C:H Lost to Catalyst	1:6	1:1	∞[a]	1:2	1:1	∞[a]	1:1

[a] ∞ means that only carbon was lost to the catalyst.

Figure 5.26c Hydrogen Balance for the Interaction of Pulses of 1:1 C_3H_4:C_3H_8 with a Chromia/K/alumina Catalyst at 550°C. (Catalyst weight = 0.2149 g).



Chapter SIX

DISCUSSION

6.1 INTRODUCTION

In Chapter Five results were presented for the interaction of dioxygen, propane, propyne and a 1:1 mixture of propane:propyne with Pt/alumina and chromia/K/alumina catalysts. The main features of the results are summarised for dehydrogenation, hydrogenation and transhydrogenation over Pt/alumina and chromia/K/alumina (Section 6.2).

Each catalyst is then discussed with regard to:

(1) oxygen adsorption on reduced catalysts

(2) dehydrogenation

(3) hydrogenation

(4) transhydrogenation.

Finally some general conclusions are drawn from the study and a brief comparison of the different catalysts is made.

6.2 SUMMARY OF HYDROCARBON ADSORPTION RESULTS

6.2.1 Pt/alumina

Dehydrogenation: Experiments PADPR.01 - PACPR.11

The product distributions for the interaction of labelled and unlabelled propane with Pt/alumina at 500°C, 550°C and 600°C were found by gas chromatography/quadrupole mass spectrometry (G.C.-M.S.) to consist of carbon monoxide, methane and trace amounts of

carbon dioxide. At 500°C trace amounts of ethane were also produced and small amounts of unreacted propane were observed. At each temperature, as pulse number increased, the amount of carbon monoxide produced decreased and the amount of methane produced increased. As temperature was increased larger amounts of carbon monoxide and smaller amounts of methane were formed.

Carbon balance calculations show that carbon was deposited on the surface of the catalyst on each propane pulse. In this instance carbon deposition increased with increase in pulse number. In general, as temperature was increased so carbon deposition increased, from 187.3 x 10^{17} atoms at 500°C (Table 5.4b) to 225.8 x 10^{17} atoms at 600°C (Table 5.6b). It was noted that when perdeutero propane and unlabelled propane were used at 600°C (Table 5.6b) a total of 225.8 x 10^{17} atoms of carbon were lost to the catalyst, whereas when (2-^{13}C)-propane and unlabelled propane were used at 600°C (Table 5.7b) a total of 59.7 x 10^{17} atoms of carbon were lost to the catalyst.

Similarly, hydrogen balance calculations show that hydrogen was lost to the catalyst on each pulse. In general, as pulse number was increased the amount of hydrogen lost to the catalyst on each pulse decreased. As temperature was increased hydrogen deposition also increased, from 587.4 x 10^{17} atoms at 500°C (Table 5.4c) to 1023.2 x 10^{17} atoms at 600°C (Table 5.6c). Again it was noted that smaller

observed. On the first pulse at 600°C, perdeutero propane, the most abundant isotopic methane was CD_2H_2. This was true of each pulse at 600°C. Significant amounts of CD_3H and CDH_3 were also observed.

At 500°C, when perdeutero propane and unlabelled propane were passed over Pt/alumina, some unreacted propane was observed. On the third pulse, perdeutero propane, C_3D_8 and $C_3D_6H_2$ were observed. On the fourth and sixth pulses, unlabelled propane, C_3H_8, C_3H_7D and $C_3D_6H_2$ were observed. On the fifth pulse, perdeutero propane, as well as C_3D_8 and $C_3D_6H_2$, C_3D_7H was observed.

When (2-^{13}C)-propane and unlabelled propane were passed over Pt/alumina at 600°C the following observations were made:

(1) No ^{13}C was detected when unlabelled propane was used as the adsorbate.

(2) When (2-^{13}C)-propane was used as the adsorbate the ratio of $^{12}CO_2$:$^{13}CO_2$ was always 1:1.

(3) When (2-^{13}C)-propane was used as the adsorbate the ratio of ^{12}CO:^{13}CO was always 2:1.

(4) When (2-^{13}C)-propane was used as the adsorbate the ratio of $^{12}CH_4$:$^{13}CH_4$ was always 2:1.

Hydrogenation: Experiments PAPRY.01 - PAPRY.03

The product distributions for the interaction of propyne with a

Transhydrogenation: Experiments PADTH.01 - PADTH.03

The product distributions for the interaction of a 1:1 mix of propyne:perdeutero propane with Pt/alumina at 500°C, 550°C and 600°C were found by G.C.-M.S. to consist of carbon monoxide, methane and small amounts of carbon dioxide. At 500°C some unreacted propane was also observed. The major product at each temperature was carbon monoxide. At 500°C, as pulse number increased the production of carbon monoxide and methane decreased and the amount of propane unreacted increased. At 550°C and 600°C as pulse number increased less carbon monoxide and more methane were produced.

Carbon balance calculations show that carbon was lost to the catalyst from each mixed gas pulse. Carbon deposition increased with increase in pulse number. As temperature was increased carbon deposition tended to decrease, from 171.0 x 10^{17} atoms at 500°C (Table 5.21b) to 117.7 x 10^{17} atoms at 600°C (Table 5.23b - after six pulses).

Hydrogen balance calculations show that, in general, hydrogen was lost to the catalyst from each mixed gas pulse. Total hydrogen deposition increased with increase in temperature, from 79.2 x 10^{17} atoms at 500°C (Table 5.21c) to 504.4 x 10^{17} atoms at 600°C (Table 5.23c - after six pulses).

At 500°C the ratio of total carbon to total hydrogen lost to the catalyst was 2:1. However, at 550°C and 600°C this figure was 1:4. At

550°C and 600°C the ratio of carbon to hydrogen lost to the catalyst decreased with increase in pulse number, from 1:7 on pulse 1 to 1:3 on pulse 6.

When the used catalysts were treated with oxygen, carbon monoxide and carbon dioxide were produced. It was also apparent that oxygen was being taken up by the catalyst.

The calculated ratio of isotopic methanes at 500°C shows that CH_4 was always the most abundant isotopic methane. As pulse number was increased the production of CD_3H, CD_2H_2 and CDH_3 increased. There was never any CD_4 detected at 500°C. As the temperature was increased to 550°C then 600°C the variety and quantity of isotopic methanes produced increased. Generally CD_2H_2 was the most abundant isotopic methane. As pulse number was increased the production of CD_2H_2 and CH_4 decreased and the production of CD_4, CD_3H and CDH_3 increased.

At 500°C mass spectra for unreacted propane show that several isotopomers of propane were present. These were C_3D_8, C_3D_7H, $C_3D_6H_2$, $C_3D_5H_3$, $C_3D_4H_4$ and $C_3D_3H_5$.

6.2.2 Chromia/alumina and Chromia/K/alumina

Dehydrogenation: Experiment CADPR.11

The product distribution for the interaction of alternate pulses of perdeutero and unlabelled propane with chromia/alumina at 500°C was

found by G.C.-M.S. to consist of carbon monoxide, methane, carbon dioxide, propene, propane and traces of ethane. Propene was only detected on unlabelled propane pulses. As a result less propane was seen by G.C. on an unlabelled propane pulse than on a perdeutero propane pulse.

Carbon balance calculations show that carbon was lost to the catalyst on each propane pulse. In general, more carbon was lost to the catalyst on an unlabelled propane pulse than on a perdeutero propane pulse. Similarly, hydrogen balance calculations show that hydrogen was lost to the catalyst on each of the six pulses. More hydrogen was deposited on the catalyst surface on an unlabelled propane pulse than on a perdeutero propane pulse. The ratio of carbon to hydrogen lost to the catalyst was lower, on average 1:4, when perdeutero propane was used than when unlabelled propane was used, on average 1:6.

When oxygen was passed over the used catalyst at 500°C small amounts of carbon monoxide and carbon dioxide were produced. It was also apparent that some of the oxygen was being adsorbed by the catalyst. After 10 pulses of oxygen 28.9% of the total carbon deposited on the surface of the catalyst had been burnt off as carbon monoxide or carbon dioxide.

Mass spectral data for the propene produced show that C_3H_5D and $C_3H_4D_2$ were produced in addition to C_3H_6. Mass spectral data for the

unreacted propane show that on the first propane pulse, perdeutero propane, C_3D_7H and $C_3D_6H_2$ were produced in addition to C_3D_8. On the other two perdeutero propane pulses, pulses 3 and 5, the only propane observed, other than C_3D_8, was C_3D_7H. On unlabelled propane pulses both C_3H_8 and C_3H_7D were observed.

Dehydrogenation: Experiments C(K)ADPR.11 - C(K)ACPR.02

The product distributions for the interaction of labelled and unlabelled propane with chromia/K/alumina at 500°C, 550°C and 600°C were found by G.C.-M.S. to consist of carbon monoxide, methane, carbon dioxide, ethane, propene and propane. At 500°C when alternate pulses of perdeutero propane and unlabelled propane were used (Table 5.9a), propene was only detected on unlabelled propane pulses. At 550°C and 600°C (Tables 5.10a and 5.11a) when alternate pulses of perdeutero propane and unlabelled propane were used propene was detected on each propene pulse. However, smaller amounts of propene were produced on perdeutero propane pulses than on unlabelled propane pulses. In experiments where (2-^{13}C)-propane was used (Tables 5.12a and 5.13a) it was noted that on (2-^{13}C)-propane pulses a decrease in the amount of propene produced, as compared to that produced on an unlabelled propane pulse, was accompanied by an increase in the production of carbon monoxide and carbon dioxide.

Carbon balance calculations show that carbon was lost to the catalyst on each propane pulse. The general trend was that carbon deposition increased with increase in temperature, from 53.5 x 10^{17} atoms at 500°C (Table 5.9b) to 94.6 x 10^{17} atoms at 600°C (Table 5.11b). When alternate pulses of perdeutero propane and unlabelled propane were used more carbon was lost to the catalyst on an unlabelled propane pulse than on a perdeutero propane pulse. When (2-^{13}C)-propane and unlabelled propane were used more carbon was lost to the catalyst on a (2-^{13}C)-propane pulse than on an unlabelled propane pulse.

Similarly, hydrogen balance calculations show that hydrogen was lost to the catalyst on each propane pulse. In general, as temperature was increased so hydrogen deposition increased, from 243.4 x 10^{17} atoms at 500°C (Table 5.9c) to 533.0 x 10^{17} atoms at 600°C (Table 5.11c). When alternate pulses of perdeutero propane and unlabelled propane were used more hydrogen was lost to the catalyst on an unlabelled propane pulse than on a perdeutero propane pulse.

The ratio of total carbon to total hydrogen lost to the catalyst varied from 1:4 at 500°C (Table 5.9d) to 1:6 at 600°C (Table 5.11d).

By pulsing oxygen over the used catalysts at the appropriate adsorption temperature it was found that only small amounts of carbon monoxide and carbon dioxide were produced. Significant amounts of oxygen were adsorbed by the catalyst samples. Only a small amount of

the total carbon deposited on the catalyst surface could be burnt off as carbon monoxide or carbon dioxide. For example, in experiment C(K)ADPR.11 after 10 pulses of oxygen at 500°C (Table 5.9e) only 6.9% of the total carbon lost to the catalyst during hydrocarbon pulsing could be burnt off as carbon monoxide or carbon dioxide.

The mass spectra for the propene and propane produced during the interaction of alternate pulses of perdeutero propane and unlabelled propane over chromia/K/alumina at 500°C showed that:

(1) Several different isotopomers of propene were produced. On pulses 2,4 and 6, unlabelled propane, $C_3H_3D_3$, $C_3H_4D_2$, C_3H_5D and C_3H_6. On pulses 4 and 6 $C_3H_2D_4$ was also produced.

(2) On perdeutero propane pulses C_3D_8 and C_3D_7H were the only isotopomers of propane observed.

(3) On unlabelled propane pulses C_3H_8 and C_3H_7D were observed. On pulse 6 $C_3H_6D_2$ was also detected.

When the temperature was increased to 550°C the following observations were made:

(1) The propene produced on perdeutero propane pulses was always C_3D_6 or C_3D_5H.

(2) On unlabelled propane pulses $C_3H_3D_3$, $C_3H_4D_2$, C_3H_5D and C_3H_6 were detected. On pulses 4 and 6 $C_3H_2D_4$ was also present.

(3) On perdeutero propane pulses the only isotopomers of propane

present were C_3D_8 , C_3D_7H and $C_3D_6H_2$.

(4) On unlabelled propane pulses C_3H_8, C_3H_7D, $C_3H_6D_2$ and $C_3H_5D_3$ were observed.

The mass spectra for the interaction of pulses of (2-^{13}C)-propane and unlabelled propane with chromia/K/alumina at 500°C and 550°C show:

(1) On unlabelled propane pulses, before any (2-^{13}C)-propane pulses, the ratio of $^{12}CH_4$:$^{13}CH_4$ was either high, 58:1 or 51:1 (at 500°C), or infinite, no $^{13}CH_4$ was observed (550°C).

(2) On (2-^{13}C)-propane pulses the ratio fell to 8:1 (at 500°C) and 2:1 or 3:1 (at 550°C).

(3) On unlabelled propane pulses, after pulses of (2-^{13}C)-propane, the ratio rose to 36:1 (at 500°C) or 15:1 (at 550°C).

(4) On (2-^{13}C)-propane pulses only (2-^{13}C)-propene and unreacted (2-^{13}C)-propane were detected.

(5) On unlabelled propane pulses only unlabelled propene and unreacted, unlabelled propane were observed.

When the catalysts used in experiments C(K)ACPR.01 and C(K)ACPR.02 were treated with oxygen the ratio of $^{12}CO_2$:$^{13}CO_2$ at 500°C (Table 5.12i) was 5:1 on oxygen pulse 1, 7:1 on oxygen pulse 6 and 45:1 on oxygen pulse 12. At 550°C (Table 5.13i) the ratio of $^{12}CO_2$:$^{13}CO_2$ was 42:1 on oxygen pulse 1 and 165:1 on oxygen pulse 6.

Hydrogenation: Experiments C(K)APRY.01 - C(K)APRY.03

The product distributions for the interaction of propyne with a chromia/K/alumina catalyst at 500°C, 550°C and 600°C were found by G.C.-M.S. to consist of carbon monoxide, methane, carbon dioxide and small amounts of propene. Ethane was also produced at 550°C. As temperature was increased, carbon monoxide and methane production increased whilst carbon dioxide and propene production decreased.

Carbon balance calculations show that carbon was lost to the catalyst from each propyne pulse. Carbon deposition was found to increase with increase in pulse number. However, total carbon deposition decreased with increase in temperature, from 358.8 x 10^{17} atoms at 500°C (Table 5.17b) to 120.9 x 10^{17} atoms at 600°C (Table 5.19b).

Hydrogen balance calculations show that, in general, hydrogen was lost to the catalyst from each propyne pulse. Within each experiment there were no specific trends in hydrogen deposition. Total hydrogen deposition decreased with increase in temperature, from 659.2 x 10^{17} atoms at 500°C (Table 5.17c) to 80.8 x 10^{17} atoms at 600°C (Table 5.19c).

The ratio of carbon to hydrogen lost to the catalyst was, in general, either 1:1 or 1:2.

Treatment of the used catalysts with oxygen produced small

amounts of carbon monoxide and large amounts of carbon dioxide. Oxygen was also found to be taken up by the catalyst. At 500°C, 45.2% of the total carbon lost to the catalyst could be burnt off as carbon monoxide or carbon dioxide (Table 5.17e). At 600°C this figure increased to 79.1% (Table 5.19e).

Hydrogenation: Experiment C(K)ADPRY.01

The product distribution for the interaction of propyne with a deuterium-reduced chromia/K/alumina catalyst at 600°C was found by G.C.-M.S. to consist of carbon monoxide, methane, carbon dioxide and small amounts of propene.

Carbon balance calculations show that carbon was lost to the catalyst from each propyne pulse. Carbon deposition increased with increase in pulse number. Similarly, hydrogen balance calculations show that hydrogen was lost to the catalyst from each propyne pulse. The ratio of total carbon to total hydrogen lost to the catalyst was found to be 1:1.

The calculated ratio of isotopic methanes for this experiment shows that on each pulse the most abundant isotopic methane was CD_2H_2. The isotopomers CDH_3 and CH_4 were not observed on any of the three pulses.

Transhydrogenation: Experiments C(K)ADTH.01 - C(K)ADTH.04

The product distributions for the interaction of a 1:1 mix of propyne:perdeutero propane with a chromia/K/alumina catalyst at 400°C, 500°C, 550°C and 600°C were found by G.C.-M.S. to consist of carbon monoxide, methane, carbon dioxide and propane. At 500°C traces of propene were observed. At 550°C and 600°C significant amounts of propene were produced. At 400°C and 500°C unreacted propane was the major product. At each of the two higher temperatures the major product was methane.

Carbon balance calculations show that carbon was lost to the catalyst from each mixed gas pulse. Most carbon was lost to the catalyst at 400°C. For the other three temperatures, when temperature was increased carbon deposition increased, from 112.3 x 10^{17} atoms at 500°C (Table 5.25b) to 196.6 x 10^{17} atoms at 600°C (Table 5.27b).

Hydrogen balance calculations show that at 400°C hydrogen was lost to the catalyst from each mixed gas pulse. At 500°C hydrogen was gained from the catalyst on all but the last pulse, where hydrogen was lost to the catalyst. At 550°C a significant amount of hydrogen was lost to the catalyst on the first pulse. On the second and third pulses small amounts of hydrogen were gained from the catalyst. On the fourth and fifth pulses hydrogen was lost to the catalyst. On the last pulse hydrogen was gained from the catalyst. Overall a small amount (49.2

x 10^{17} atoms) of hydrogen was lost to the catalyst. At 600°C hydrogen was lost to the catalyst from each mixed gas pulse.

The ratios of total carbon to total hydrogen lost to the catalyst varied from 1:2 at 400°C to ∞ (only carbon lost to the catalyst) at 500°C to 1:3 at 550°C to 1:4 at 600°C.

When the catalysts used at 400°C, 500°C and 600°C were treated with oxygen, carbon monoxide and carbon dioxide were produced. Oxygen was also taken up by the catalyst. At 400°C (Table 5.24e) 39.0% of the carbon deposited on the catalyst during hydrocarbon pulsing could be burnt off as carbon monoxide or carbon dioxide. This figure fell to 20.9% at 600°C (Table 5.27e).

Calculated ratios of isotopic methane show that, in general, CH_4 was the most abundant methane. As temperature was increased the variety of isotopic methanes increased. At 500°C (Table 5.25f) CH_4 was the most abundant isotopic methane and small amounts of CD_4, CD_3H, CD_2H_2 and CDH_3 were also observed. At 600°C (Table 5.27f) equal amounts of CD_2H_2, CDH_3 and CH_4 were observed and only small amounts of CD_4 and CD_3H were detected.

Mass spectral data for the propene produced at 500°C and 550°C shows that both C_3H_6 and C_3H_5D were produced. At 600°C, in addition to C_3H_6 and C_3H_5D, $C_3H_4D_2$ was produced.

At 400°C and 500°C C_3D_8, C_3D_7H and $C_3D_6H_2$ were observed in

the mass spectra for unreacted propane. At 550°C only C_3D_8 and C_3D_7H were observed. At 600°C C_3D_8, C_3D_7H and $C_3D_6H_2$ were detected.

Transhydrogenation: Experiments C(K)ATH.01 and C(K)ATH.02

The product distributions for the interaction of 25 mbar (Experiment C(K)ATH.01) and 50 mbar (Experiment C(K)ATH.02) pulses of a 1:1 mix of propyne:propane with chromia/K/alumina at 550°C were found by G.C.-M.S. to consist of carbon monoxide, carbon dioxide, propene and propane. It was noted that on the first three pulses of experiment C(K)ATH.01 no propene or propane were produced (Table 5.28a) but large amounts of carbon dioxide were produced. Comparing the last pulse of each experiment it was possible to say that doubling the pulse size produces almost double the amount of propene (13.6×10^{17} molecules compared with 8.3×10^{17} molecules). Production of C_1's remained approximately constant, whilst much more propane remained unreacted in the experiment with the larger pulse size.

Carbon balance calculations show that carbon was lost to the catalyst on each mixed gas pulse. However, hydrogen balance calculations show that on some pulses hydrogen was lost to the catalyst whilst on others hydrogen was gained from the catalyst.

6.3 Pt/ALUMINA

6.3.1 Dioxygen Adsorption

When dioxygen was passed over reduced Pt/alumina (6% H_2/N_2 at 600°C for 15 minutes) at 600°C, the average ratio of adsorbed oxygen to platinum in the sample was 0.97:1.00. If the starting oxide is taken as PtO and the oxygen adsorbed fully replaced all that was removed during the reduction process, then the reduced species is Pt metal.

6.3.2 Dehydrogenation

On examining the product distributions for the interaction of labelled and unlabelled propane with Pt/alumina at 500°C, 550°C and 600°C it is clear that initially the main reaction taking place was dissociation of propane. As carbon monoxide and carbon dioxide were also produced the catalyst must still have been undergoing reduction. As pulse number increased at a particular temperature, production of carbon monoxide decreased suggesting that there was less available oxygen and that the catalyst was almost completely reduced. As temperature was increased larger quantities of carbon monoxide were produced indicating that more oxygen was available from the catalyst at higher temperatures.

Several significant differences were noted when (2-^{13}C)-propane was used as the labelled gas over a Pt/alumina catalyst at 600°C (Section

6.2). As larger amounts of carbon monoxide and carbon dioxide were produced when (2-^{13}C)-propane was used, it was thought likely that either the catalyst was reduced to a lesser extent or that the (2-^{13}C)-propane contained an impurity. As the amount of carbon monoxide produced on the first pulse was in fact smaller when (2-^{13}C)-propane was used, as opposed to when perdeutero propane was used, it was concluded that the catalyst was in fact reduced to a slightly greater extent. The difference in results was therefore attributed to an impurity in the (2-^{13}C)-propane.

Carbon and hydrogen balance calculations showed that during each experiment carbon and hydrogen were lost to the catalyst. The higher the temperature the greater was the extent of carbon and hydrogen deposition. As a result of the increased production of carbon monoxide and carbon dioxide when (2-^{13}C)-propane was used, carbon deposition was significantly less than during the similar experiment using perdeutero propane. In turn, this led to smaller ratios of carbon to hydrogen lost to the catalyst. The total ratio of carbon to hydrogen lost to the catalyst was 1:4 when perdeutero propane was used and 1:15 when (2-^{13}C)-propane was used.

When alternate pulses of perdeutero propane and unlabelled propane were passed over freshly reduced catalyst samples at 500°C, 550°C and 600°C the only hydrocarbon product was methane, with the

exception of the later pulses at 500°C when small amounts of propane remained unreacted. Analysis of the isotopic composition of the methane product from each pulse revealed that, even after flushing with helium at the reaction temperature, a considerable quantity of hydrogen from the reduction process was retained by the catalyst. This was apparent because on the first pulse, perdeutero propane, the most abundant isotopic methane tended to be CH_4. The range of methanes produced on each pulse suggests that there was considerable isotopic mixing on the surface of the catalyst. Isotopic mixing appeared to increase with increase in temperature. This shows that not only was there extensive isotopic mixing with the "hydrogen" retained from the reduction process, but also with "hydrogen" deposited on the catalyst from the propane itself.

Though no isotopic mixing was observed in the experiment carried out using (2-^{13}C)-propane at 600°C, a similar experiment carried out by an earlier investigator of this reaction[65] showed that there was considerable isotopic mixing at 500°C, independent of whether the pulse was (2-^{13}C)-propane or unlabelled propane. From the results of that experiment the conclusion drawn was that, whilst there was considerable isotopic mixing of the surface carbon pool, the isotopic mixing was not totally random.

When (2-^{13}C)-propane and unlabelled propane were used some

interesting mass spectral data were produced. When (2-^{13}C)-propane was used as the adsorbate:-

(1) the ratio of $^{12}CO_2$:$^{13}CO_2$ was always 1:1

(2) the ratio of ^{12}CO:^{13}CO was always 2:1

(3) the ratio of $^{12}CH_4$:$^{13}CH_4$ was always 2:1.

A possible explanation for this is that a propane molecule can be adsorbed onto the catalyst surface in such a way that carbons 1, 2 and 3 are equally likely to give carbon monoxide or methane. However, this can not be the case for carbon dioxide. Also, the ratios show that carbon monoxide is not an intermediate in the formation of carbon dioxide. If it were the ratio of ^{12}CO:^{13}CO and $^{12}CO_2$:$^{13}CO_2$ would be the same.

One possibility is that carbons 1 and 2, or carbons 2 and 3, react to produce carbon dioxide and the other carbon stays on the surface of the catalyst. As carbon monoxide is not an intermediate, the carbon must have picked up both oxygens simultaneously. This result is similar to that found by Jackson *et al.*[66] when they investigated the hydrogenation of carbon monoxide and carbon dioxide and found that carbon dioxide hydrogenation did not go through carbon monoxide.

As perdeutero propane and (2-^{13}C)-propane were used as tracers it was possible to investigate the composition and reactivity of the carbon and hydrogen laid down during the initial stages of the propane

dehydrogenation reaction. As stated earlier, during each experiment appreciable amounts of both carbon and hydrogen were deposited on the surface of the catalyst from each pulse of propane. This resulted in the formation of a carbonaceous residue (C_xH_y) on the catalyst surface. However, analysis of the isotopic composition of the methane product from each pulse revealed that, even after flushing with helium at the reaction temperature, a considerable quantity of hydrogen from the reduction process was retained by the catalyst, thereby not permitting calculation of the average composition of the carbonaceous deposit, C_xH_y.[67]

Pulsing dioxygen over the used catalyst charges produced significant quantities of carbon monoxide and carbon dioxide. It was also apparent that oxygen was being taken up by the catalyst. It is of interest to note that the dioxygen "burn off" resulted in removal of only a small fraction of the catalyst carbon. As experiment temperature was increased, progressively less of the carbon deposited during the reaction could be removed by high temperature dioxygen treatment.

6.3.3 Hydrogenation

On investigating the product distributions for the interaction of propyne with a Pt/alumina catalyst at 500°C, 550°C and 600°C the only observed reaction was dissociation of propyne. As expected

considerably more carbon monoxide was produced when propyne was used than when propane was used.

Calculations showed that both carbon and hydrogen were deposited on the catalyst surface during each reaction. Total carbon deposition was found to be less when propyne was used than when propane was used. Similarly hydrogen deposition was lower when propyne was used rather than propane.

The above results are entirely expected as experiments were carried out approximately 300°C higher than the temperature at which hydrogenation activity of supported platinum is at a maximum. For example, Jackson and Kelly[56] found 100% selectivity at total conversion of propyne at 250°C.

When the catalyst used at 500°C was treated with dioxygen, 93.4% of the carbon deposited during the reaction could be burnt off as carbon monoxide or carbon dioxide. This is almost the opposite effect of that observed when the catalysts used for propane dehydrogenation were treated with dioxygen. A possible explanation for this is that the carbonaceous overlayer formed during hydrogenation was hydrogen deficient - the ratio of total carbon:total hydrogen lost to the catalyst was 1:1 - and therefore was more reactive. On the other hand, the carbonaceous overlayer formed during the dehydrogenation of propane contained significantly more hydrogen - the ratio of total carbon:total

hydrogen lost to the catalyst was 1:3 - and therefore was less reactive.

6.3.4 Transhydrogenation

As for propane and propyne, when a 1:1 mixture of perdeutero propane and unlabelled propyne was passed over a Pt/alumina catalyst at 500°C, 550°C and 600°C the major reaction was dissociation of the hydrocarbons. At 500°C a significant amount of perdeutero propane remained unreacted. By the sixth pulse 70% of the perdeutero propane remained unreacted. This indicates that the propyne was preferentially adsorbed on the catalyst surface and could therefore undergo dissociation. In the earlier stages of the reaction, when more sites were available, both propyne and propane could be adsorbed on the catalyst surface and hence undergo dissociation.

As pulse number increased more reactive sites were blocked as carbon and hydrogen were deposited on the surface of the catalyst. As these sites were blocked the activity of the catalyst decreased.

Less carbon was lost to the catalyst during transhydrogenation reactions, than during the corresponding dehydrogenation and hydrogenation reactions. However, more hydrogen was lost to the catalyst during transhydrogenation reactions than during corresponding hydrogenation reactions. In turn, more hydrogen was lost to the catalyst during dehydrogenation reactions than during the corresponding

transhydrogenation reactions.

Figure 6.1 shows the calculated ratio of isotopic methanes for (a) dehydrogenation of alternate pulses of perdeutero propane and unlabelled propane and (b) transhydrogenation of pulses of a 1:1 mixture of perdeutero propane and propyne over a Pt/alumina catalyst at 500°C. It is immediately clear that during dehydrogenation a random mixture of all isotopic methanes was formed. However, during transhydrogenation CH_4 was formed preferentially on all six pulses. This suggests that methane was formed from propyne not perdeutero propane during transhydrogenation. Similar results were found at 550°C and 600°C.

High temperature dioxygen treatment of the catalysts used for transhydrogenation produced carbon monoxide and carbon dioxide. As reaction temperature was increased the fraction of carbon which could be burnt off the catalyst decreased - from 93.0% at 500°C to 27.1% at 600°C. A possible explanation for the large amount of carbon which could be burnt off the catalyst used at 500°C is that the carbon was produced mainly from propyne. In the corresponding dehydrogenation reaction 45.3% of the carbon deposited during the reaction could be burnt off the catalyst, whereas in the corresponding hydrogenation reaction 93.4% of the carbon deposited during the reaction could be burnt off the catalyst. This also appears to be related to the ratio of total carbon to total hydrogen lost to the catalyst. At 500°C the ratio of total

Figure 6.1(a) Calculated Ratio of Isotopic Methanes Produced During Dehydrogenation of Alternate Pulses of Perdeutero and Unlabelled Propane over Pt/alumina at 500°C.

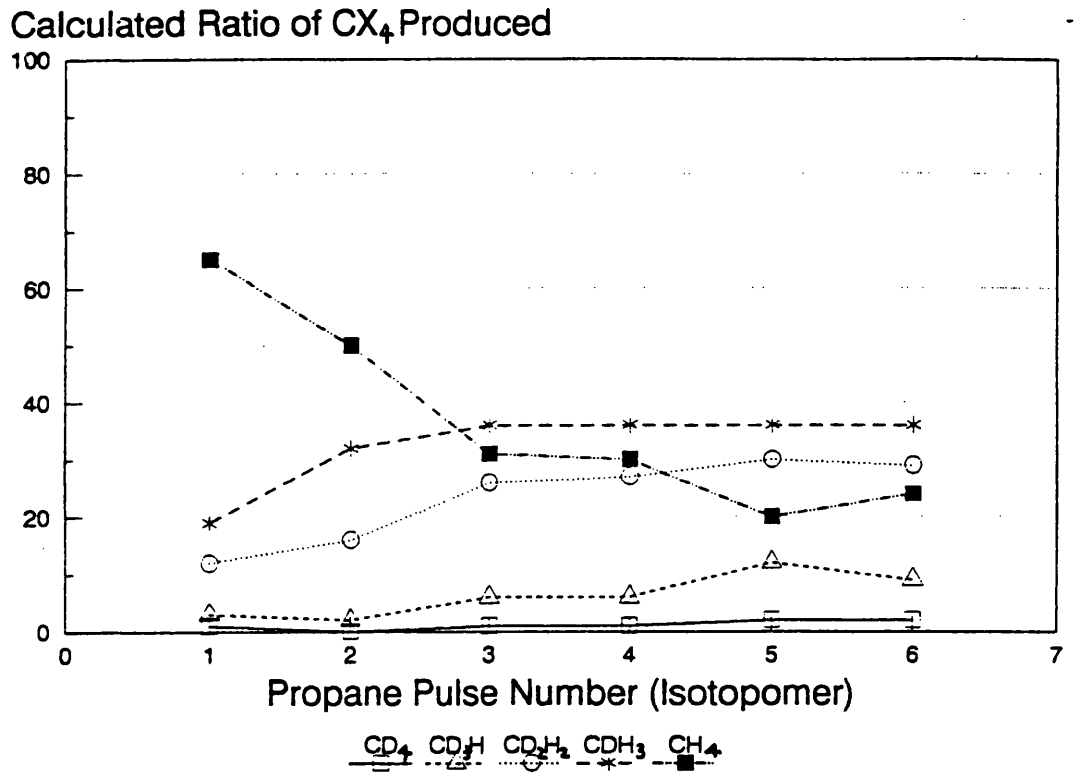
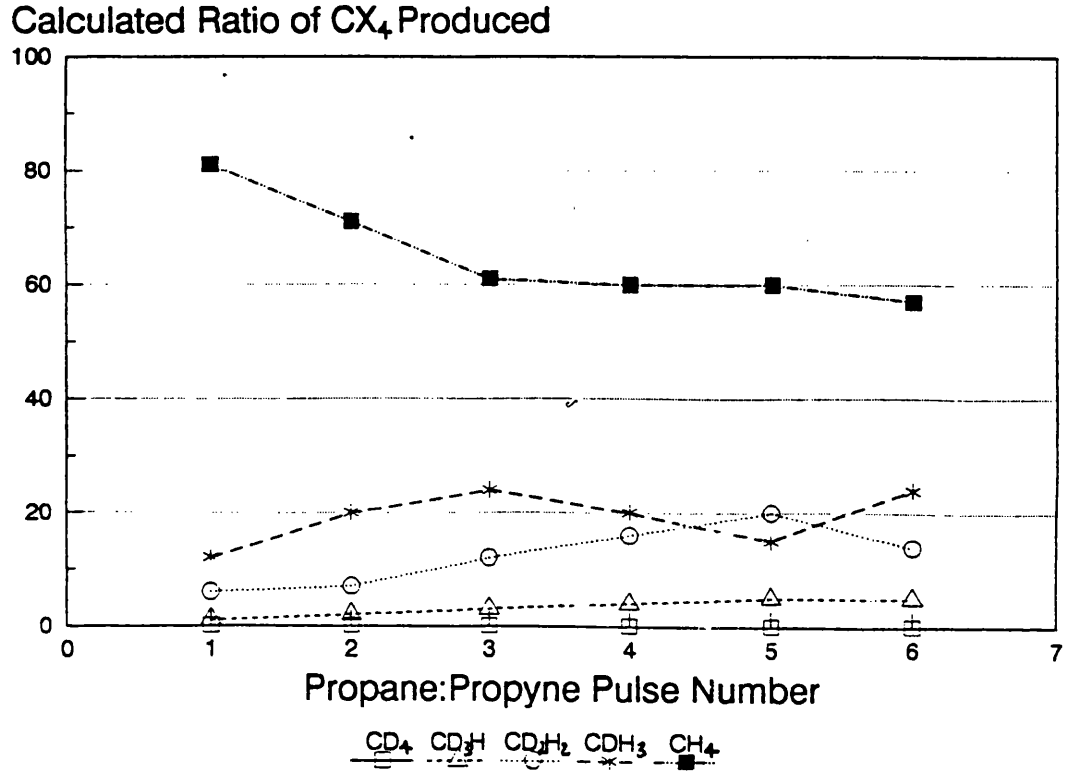


Figure 6.1b Calculated Ratio of Isotopic Methanes Produced During Transhydrogenation of Pulses of a 1:1 Mixture of Perdeutero Propane and Unlabelled Propyne over Pt/alumina at 500°C.



carbon to total hydrogen lost to the catalyst during dehydrogenation was 1:3; during hydrogenation this figure was 1:1; and during transhydrogenation the ratio was 2:1. From these figures it appears that when the carbonaceous overlayer contains large amounts of hydrogen it is more difficult to remove this carbonaceous overlayer by high temperature dioxygen treatment.

6.4 CHROMIA/ALUMINA AND CHROMIA/K/ALUMINA

6.4.1 Dioxygen Adsorption

When dioxygen was passed over reduced chromia/alumina (6% H_2/N_2 at 600°C for 15 minutes) at 600°C, the average ratio of adsorbed oxygen to chromium in the sample was 0.24:1.00. When dioxygen was passed over reduced chromia/K/alumina (6% H_2/N_2 at 600°C for 15 minutes) at 600°C, the average ratio of adsorbed oxygen to chromium in the sample was 0.22:1.00. In both cases if the starting oxide is taken as Cr_2O_3 and the oxygen adsorbed fully replaced all that was removed during the reduction process, then the reduced species is $CrO_{1.27}$.

6.4.2 Dehydrogenation

When alternate pulses of perdeutero propane and unlabelled propane were passed over a chromia/alumina or chromia/K/alumina catalyst at 500°C, two main reactions took place: some of the propane

dissociated to form carbon monoxide, methane and carbon dioxide and a carbonaceous overlayer on the catalyst and some of the propane was dehydrogenated to propene. At 500°C no propene was produced when perdeutero propane was used as the adsorbate.

When alternate pulses of perdeutero propane and unlabelled propane were passed over a chromia/K/alumina catalyst at 550°C and 600°C the same two reactions took place. However, it was noted that, at these two higher temperatures, propene was produced on perdeutero propane pulses as well as on unlabelled propane pulses. Smaller amounts of propene were produced when perdeutero propane was used than when unlabelled propane was used. Table 6.1 shows the amount of propene produced, as a percentage of the C_3-components in the product mixture, for each of the dehydrogenation experiments over chromia/alumina and chromia/K/alumina.

These results show that there is a significant isotope effect in propane dehydrogenation over chromia/alumina and chromia/K/alumina. At 500°C this isotope effect is large enough to prevent formation of propene from perdeutero propane. At 550°C and 600°C, the isotope effect is clearly visible in that more propene is produced on an unlabelled propane pulse than on a perdeutero propane pulse.

Table 6.1 Propene Produced, as a Percentage of the C_3-Components in the Product Mixture, During the Dehydrogenation of Propane over Chromia/alumina and Chromia/K/alumina.

PULSE	Experiment CADPR.11 500°C	Experiment C(K)ADPR.11 500°C	Experiment C(K)ADPR.12 550°C	Experiment C(K)ADPR.13 600°C
1(C_3D_8)	0.0	0.0	35.9	42.5
2(C_3H_8)	28.9	29.2	44.9	60.9
3(C_3D_8)	0.0	0.0	29.8	41.0
4(C_3H_8)	30.7	36.3	44.7	60.5
5(C_3D_8)	0.0	0.0	30.5	40.4
6(C_3H_8)	33.8	28.0	44.5	59.7

STANOPT thermodynamic equilibrium calculations[68] show that at 1 atmosphere pressure and 500°C the propene mole percent of C_3-components, during the dehydrogenation of propane, is approximately 18%. At 550°C this figure is approximately 33%. It would appear that the propene-propane equilibrium is being surpassed during these experiments. This is not surprising as flow conditions are being used.

In similar experiments using unlabelled propane and (2-^{13}C)-propane it was noted that when (2-^{13}C)-propane was used there was a decrease in the amount of propene produced, as compared to that produced on an unlabelled propane pulse. This decrease in production of propene was accompanied by an increase in the formation of carbon monoxide and carbon dioxide. This appears to confirm the earlier

assumption (Section 6.3.1) that there was an impurity in the (2-^{13}C)-propane. Table 6.2 shows that the position of the propene-propane equilibrium was not significantly affected by this impurity.

Table 6.2 Propene Produced, as a Percentage of C_3-Components in the Product Mixture, During Dehydrogenation of Unlabelled Propane and (2-^{13}C)-Propane over Chromia/K/alumina.

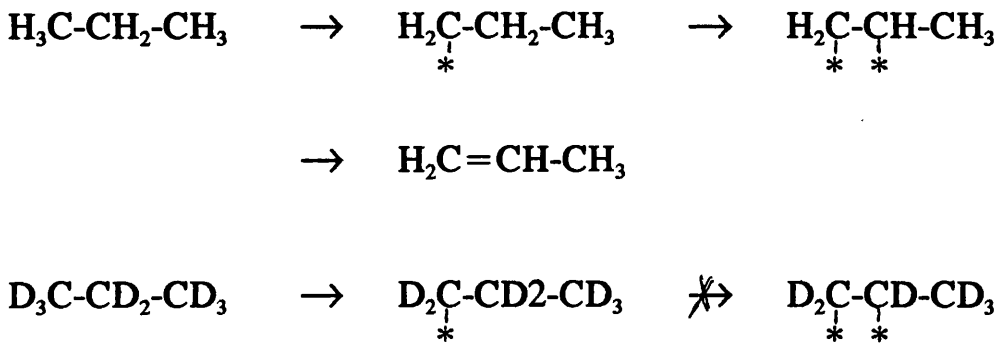
PULSE	Experiment C(K)ACPR.01 500°C	PULSE	Experiment C(K)ACPR.02 600°C
1	34.0	1	43.9
2	33.4	2	45.2
3(2-^{13}C)	33.5	3(2-^{13}C)	43.7
4(2-^{13}C)	28.1	4(2-^{13}C)	42.4
5(2-^{13}C)	28.0	5	45.3
6	30.4	6	44.7
7	29.9		

These figures suggest that the same equilibrium position is attained regardless of whether unlabelled propane or (2-^{13}C)-propane is used.

Mass spectral data for the dehydrogenation of alternate pulses of perdeutero propane and unlabelled propane over chromia/alumina and chromia/K/alumina at 500°C showed that on a perdeutero propane pulse only C_3D_7H and C_3D_8 were observed. However, on an unlabelled propane pulse C_3H_8, C_3H_7D and $C_3H_6D_2$ were observed. Various

propenes, $C_3H_3D_3$, $C_3H_4D_2$, C_3H_5D and C_3H_6, were also observed on unlabelled propane pulses. This has led to the conclusion that perdeutero propane can exchange only one deuterium at 500°C. The mechanism shown in Figure 6.2 has been proposed to account for this. Unlabelled propane can be adsorbed by the catalyst losing either one hydrogen atom or two hydrogen atoms. Perdeutero propane cannot undergo this second step, therefore perdeutero propene and $C_3D_6H_2$ are not observed.

Figure 6.2 Proposed Mechanism for Dehydrogenation of Propane on Chromia/alumina and Chromia/K/alumina.



As temperature was increased it was possible for perdeutero propane to lose a second deuterium and hence form perdeutero propene and various propanes - C_3D_7H and $C_3D_6H_2$.

It can be concluded that the rate determining step in the dehydrogenation of propane over chromia/alumina and

chromia/K/alumina is

$$C_3H_8\ (ads) \rightarrow C_3H_6\ (ads) + H_2\ (ads).$$

This conclusion agrees with that reached by Suzuki and Kaneko,[37] who found the same rate determining step for the dehydrogenation of propane.

During each dehydrogenation experiment over chromia/alumina and chromia/K/alumina both carbon and hydrogen were deposited on the surface of the catalyst. Clearly, because various isotopomers of propene and propane were produced during alternate pulses of perdeutero propane and unlabelled propane, there was mixing of hydrogen on the catalyst surface. During experiments using (2-^{13}C)-propane determination of the ^{12}C:^{13}C ratio in the methane yield showed that there was considerable isotopic mixing of carbon independent of whether the pulse was (2-^{13}C)-propane or unlabelled propane. For example, at 550°C, on pulses 1 and 2, unlabelled propane, no ^{13}C was observed. On pulses 3 and 4, (2-^{13}C)-propane, the ratio of $^{12}CH_4$:$^{13}CH_4$ was 2:1 and 3:1 respectively. However, on pulses 5 and 6, unlabelled propane, the ratio of $^{12}CH_4$:$^{13}CH_4$ was 15:1 and 24:1 respectively, suggesting that a significant amount of ^{13}C could be removed from the catalyst on later pulses.

By pulsing oxygen over the catalysts used during the

dehydrogenation experiments only a small amount of the carbonaceous deposit could be removed. for experiments using (2-^{13}C)-propane the ratio of $^{12}CO_2$:$^{13}CO_2$ in the product of dioxygen burn off was determined. This ratio varied considerably, from 5:1 on dioxygen pulse 1, to 7:1 on dioxygen pulse 6, to 45:1 on dioxygen pulse 12 at 500°C. From these figures it is also clear that there is considerable isotopic mixing of the surface carbon pool.

An attempt has been made to model the dehydrogenation reaction. Assuming that propane dehydrogenation does not involve a concerted mechanism, a sequential model has been devised (Figure 6.3).

Figure 6.3 Sequential Model for Dehydrogenation of Propane (X = H or D).

$$C_3X_8 \rightarrow C_3X_6 + X_2 \quad (1)$$

$$C_3X_8 \rightarrow 2CX_4 + C \quad (2)$$

$$C_3X_8 \rightarrow CX_4 + C_2X_4 \quad (3)$$

$$C_3X_8 \rightarrow 3C + 4X_2 \quad (4)$$

$$C_2X_4 + X_2 \rightarrow C_2X_6$$

$$C_3X_8 + O_2 \rightarrow 3CO + 4X_2$$

$$C_3X_8 + O_2 \rightarrow 3CO_2 + 4X_2$$

Obviously, propane can give propene and dihydrogen. Propane can also give methane and carbon, methane and ethene, carbon and dihydrogen. Ethene could react with dihydrogen to give ethane. Finally, carbon monoxide and carbon dioxide could be produced by reaction of propane with catalyst oxygen. The results of each of the dehydrogenation experiments were used to test the model.

All propene produced must come from equation (1) so it is unique. The amount of ethane produced is known, again it is unique. The amount of methane which comes from equation (3) can therefore be calculated. The remaining methane obviously comes from equation (2). Carbon is produced in equations (2) and (4). The amount of carbon produced in equation (2) is known so the amount of carbon which comes from equation (4) can be calculated. Therefore, the amount of hydrogen which comes from equation (4) can also be calculated. Carbon monoxide and carbon dioxide are both unique, so the amount of propane used in their formation can be calculated. By subtracting the amounts of propane reacted in each of these equations from the amount of propane used in the pulse the amount of propane which remains unreacted can be calculated. This figure, along with the calculated amount of hydrogen produced are used to test the model.

The results of each experiment have been shown to fit the model. To illustrate this the figures for experiment C(K)ADPR.11 are given in

Table 6.3(a) and the figures for experiment C(K)ACPR.02 are given in Table 6.3(b).

Table 6.3 (a) Reaction Modelling: Experiment C(K)ADPR.11

PULSE	C_3X_8 Unreacted (mols. x 10^{17})		X Produced (atoms x 10^{17})	
	MODEL	ACTUAL	MODEL	ACTUAL
1(C_3D_8)	33.0	32.9	24.1	24.4
2(C_3H_8)	22.2	22.1	55.0	55.4
3(C_3D_8)	33.4	33.3	20.8	21.2
4(C_3H_8)	19.4	19.3	66.0	66.8
5(C_3D_8)	33.8	33.9	17.6	16.8
6(C_3H_8)	22.1	22.1	58.8	58.8

(b) Reaction Modelling: Experiment C(K)ACPR.02

PULSE	C_3X_8 Unreacted (mols. x 10^{17})		X Produced (atoms x 10^{17})	
	MODEL	ACTUAL	MODEL	ACTUAL
1	15.9	16.0	80.0	79.4
2	11.6	11.5	137.0	137.8
3(2-^{13}C)	7.6	7.6	190.6	190.6
4(2-^{13}C)	9.5	9.5	134.6	134.4
5	17.4	17.5	59.2	58.4
6	17.8	17.6	58.2	58.6

Clearly figures calculated from the model are very similar to

experimental results, suggesting that the model is correct.

6.4.3 Hydrogenation

When propyne was passed over a chromia/K/alumina catalyst at 500°C, 550°C and 600°C the main reaction which took place was dissociation of propyne. At each temperature there was evidence that a small amount of propyne was hydrogenated to give propene.

Significantly more carbon and hydrogen were lost to the catalyst during these hydrogenation reactions than during the equivalent dehydrogenation reactions. The ratio of total carbon to total hydrogen lost to the catalyst was 1:1 or 1:2 during hydrogenation whereas during dehydrogenation this ratio was typically 1:5. Clearly the carbonaceous overlayer is hydrogen deficient during hydrogenation reactions.

When dioxygen was passed over the used hydrogenation catalysts at the appropriate adsorption temperature significant amounts of carbon could be removed. After hydrogenation at 550°C, 34.4% of the carbon lost to the catalyst could be removed by dioxygen treatment. In comparison, only 1.9% of the carbon lost to the catalyst during dehydrogenation at 550°C could be removed by dioxygen treatment. From this it has been concluded that when the carbonaceous overlayer is hydrogen-rich it is more difficult to remove from the catalyst than when it is hydrogen deficient.

When a chromia/K/alumina catalyst was reduced with deuterium, instead of 6% dihydrogen/dinitrogen, then treated with propyne at 600°C, the calculated ratio of isotopic methanes produced in the experiment shows that there was considerable isotopic mixing on the surface of the catalyst. Even though unlabelled propyne was used as the adsorbate, CDH_3 and CH_4 were never observed during the experiment. This suggest that not only was there isotopic mixing on the surface of the catalyst, but there was also isotopic mixing between the surface of the catalyst and the adsorbate.

6.4.4 Transhydrogenation

When a 1:1 mixture of perdeutero propane and unlabelled propyne was passed over a chromia/K/alumina catalyst at 400°C, 500°C, 550°C and 600°C the main reaction which took place was dissociation of the hydrocarbons. By pulse 2 at 400°C it was apparent that most of the perdeutero propane remained unreacted. One possible explanation for this is that as the number of active sites decreased, due to the formation of a carbonaceous overlayer, propyne was preferentially adsorbed and could therefore undergo dissociation. Mass spectral data supports this explanation - the most abundant isotopic methane was always CH_4, implying that methane was formed from unlabelled propyne not perdeutero propane.

At 500°C traces of propene were observed. However, the main reaction which took place was still dissociation of propyne. At 550°C and 600°C dissociation of propyne was accompanied by dehydrogenation of propane and hydrogenation of propyne. Though yields of propene were lower than in the corresponding dehydrogenation reactions, the percentage of propene contained in the C_3-component of the product mixture was greater during transhydrogenation experiments than during dehydrogenation experiments. Table 6.4 shows the amount of propene produced, as a percentage of C_3-components in the reaction mixture, for each of the transhydrogenation experiments using a 1:1 mixture of perdeutero propane and unlabelled propyne over chromia/K/alumina.

Table 6.4 Propene Produced, as a Percentage of C_3-Components in the Product Mixture, for Experiments C(K)ADTH.01 - C(K)ADTH.04.

PULSE	Experiment C(K)ADTH.01 400°C	Experiment C(K)ADTH.02 500°C	Experiment C(K)ADTH.03 550°C	Experiment C(K)ADTH.04 600°C
1(C_3H_4/C_3D_8)	0.0	0.0	50.6	0.0
2(C_3H_4/C_3D_8)	0.0	0.0	51.0	0.0
3(C_3H_4/C_3D_8)	0.0	0.0	53.9	89.3
4(C_3H_4/C_3D_8)	0.0	0.0	57.3	86.1
5(C_3H_4/C_3D_8)	0.0	0.0	57.8	83.6
6(C_3H_4/C_3D_8)	0.0	0.0	57.4	95.6

Results at 400°C and 500°C are entirely as expected. In order for transhydrogenation to occur it must be possible to dehydrogenate the alkane and hydrogenate the alkyne. However, during dehydrogenation experiments (Section 6.4.1) it was found that perdeutero propane could not be dehydrogenated at 500°C. Therefore, as perdeutero propane cannot be dehydrogenated, transhydrogenation cannot occur. At 550°C and 600°C conditions clearly favour formation of propene from propane.

Mass spectral data for the experiments carried out at 550°C and 600°C show that methane is predominantly produced by dissociation of unlabelled propyne. On nearly every pulse the most abundant isotopic methane was CH_4. At 600°C the quantities of other isotopic methanes, especially CH_2D_2 and CH_3D, had increased, suggesting that isotopic mixing increased with increase in temperature. A similar trend was observed when Pt/alumina was used for dehydrogenation of propane (Section 6.3.1). Mass spectral data shows that a range of propenes were produced. The most abundant being C_3H_6, C_3H_5D and $C_3H_4D_2$. This suggests that a significant amount of the propene produced was formed by hydrogenation of unlabelled propyne rather than by dehydrogenation of perdeutero propane.

During each experiment carbon and hydrogen were lost to the surface of the catalyst, forming a carbonaceous overlayer. Larger amounts of the carbonaceous overlayer could be removed by high

temperature dioxygen treatment than could be removed in the corresponding dehydrogenation reactions. When the ratio of total carbon to total hydrogen lost to the catalyst is considered it is clear that during transhydrogenation a hydrogen-deficient carbonaceous overlayer was formed. Significant amounts of this carbonaceous overlayer could be removed by high temperature dioxygen treatment, confirming the earlier observation that when the carbonaceous overlayer is hydrogen-rich it is more difficult to remove from the catalyst than when it is hydrogen-deficient.

When a 1:1 mixture of unlabelled propyne and unlabelled propane was passed over chromia/K/alumina at 550°C two main reactions took place - dissociation of the hydrocarbons and formation of propene. Table 6.5 shows the amount of propene produced, as a percentage of the C_3-components in the product mixture, for transhydrogenation reactions using a 1:1 mixture of propane and propyne over chromia/K/alumina.

The percentage of propene found in the C_3-component of the product mixture is approximately the same when either a 1:1 mixture of unlabelled propyne and perdeutero propane or a 1:1 mixture of unlabelled propyne and unlabelled propane is used. This suggests that there is no deuterium-hydrogen effect during transhydrogenation over chromia/K/alumina at 550°C. A deuterium-hydrogen effect was present during dehydrogenation of propane over chromia/K/alumina at 550°C

though only to a limited extent (Section 6.4.1).

Table 6.5 Propene Produced, as a Percentage of C_3-Components in the Product Mixture, For Experiments C(K)ATH.01 and C(K)ATH.02.

PULSE	Experiment C(K)ATH.01 550°C (Pulse size 36.0 x 10^{17} molecules)	Experiment C(K)ATH.02 550°C (Pulse size 72.0 x 10^{17} molecules)
1(C_3H_4/C_3H_8)	0.0	49.0
1(C_3H_4/C_3H_8)	0.0	41.0
1(C_3H_4/C_3H_8)	0.0	38.8
1(C_3H_4/C_3H_8)	55.2	41.0
1(C_3H_4/C_3H_8)	52.6	38.5
1(C_3H_4/C_3H_8)	50.9	37.6

Increasing the pulse size without increasing the volume of catalyst, and hence the number of active sites, resulted in formation of larger amounts of propene. However, the percentage of propene in the C_3-component of the product mixture was smaller when the larger pulse was used. When the pulse size was 36.0 x 10^{17} molecules the amount of propene produced, as a percentage of C_3-components in the product mixture was approximately 53%. When the pulse size was doubled this figure fell to approximately 40%. The most obvious explanation for this is that a larger amount of propane remained unreacted at the larger pulse

size. Table 6.6, which shows the amount of propane in the product mixture as a percentage of the amount of propane used in each pulse, confirms this.

Table 6.6 Amount of Propane in the Product Mixture as a Percentage of Propane Used in Each Pulse During Transhydrogenation of Propane over Chromia/K/alumina at 500°C.

PULSE	% Unreacted Propane	
	Experiment C(K)ATH.01	Experiment C(K)ATH.02
1(C_3H_4/C_3H_8)	0.0	22.2
1(C_3H_4/C_3H_8)	0.0	49.2
1(C_3H_4/C_3H_8)	0.0	58.3
1(C_3H_4/C_3H_8)	33.3	31.1
1(C_3H_4/C_3H_8)	40.0	59.2
1(C_3H_4/C_3H_8)	44.4	62.8

Obviously, the fact that a larger amount of propane remains unreacted will affect the percentage of propene in the C_3-component of the product mixture in such a way that it appears the formation of propene is inhibited.

6.5 CONCLUSIONS

6.5.1 Pt/alumina

From dehydrogenation, hydrogenation and transhydrogenation experiments on Pt/alumina in the temperature range 500°C to 600°C the following conclusions were drawn:

(1) The main reaction taking place is dissociation of propane and subsequent formation of a carbonaceous deposit, containing both carbon and hydrogen, on the catalyst surface.

(2) Within the carbonaceous deposit there is mixing of both carbon and hydrogen as revealed by isotopic tracer techniques.

(3) Only a fraction of the carbon laid down on the catalyst during an experiment can be removed by high temperature dioxygen treatment.

(4) The amount of carbon which can be removed is dependent on the ratio of total carbon to total hydrogen lost to the catalyst during a particular experiment. When the carbonaceous layer contains large amounts of hydrogen it is more difficult to remove the carbonaceous overlayer by high temperature dioxygen treatment.

6.5.2 Chromia/alumina and Chromia/K/alumina

From investigations of dehydrogenation of propane on chromia/alumina and chromia/K/alumina the following conclusions were

drawn:

(1) There is a significant deuterium-hydrogen isotope effect. At 500°C this isotope effect is large enough to prevent formation of propene from perdeutero propane. At 550°C and 600°C the isotope effect is still present, but not so significant.

(2) The rate determining step is

$$C_3H_8\ (ads) \rightarrow C_3H_6\ (ads) + H_2\ (ads).$$

(3) In addition to dehydrogenation of propane to propene, some dissociation of propane occurs. This dissociation results in the formation of a carbonaceous overlayer, containing carbon and hydrogen, on the surface of the catalyst.

(4) Within the carbonaceous deposit there is mixing of both carbon and hydrogen as revealed by isotopic tracer studies.

(5) A sequential model can be devised for the reaction.

From investigations of hydrogenation of propyne on chromia/K/alumina the following conclusion was drawn:

The main reaction taking place is dissociation of propyne and subsequent formation of a carbonaceous overlayer on the catalyst surface.

Transhydrogenation does occur on chromia/K/alumina in the temperature range 550°C to 600°C. During transhydrogenation experiments the following observations were made:

(1) Propyne is hydrogenated to propene and propane is dehydrogenated to propene.

(2) Due to dissociation of the hydrocarbons a carbonaceous overlayer is formed on the catalyst surface.

(3) Isotopic tracer techniques revealed there is isotopic mixing within the carbonaceous overlayer.

During the three types of experiment, dehydrogenation, hydrogenation and transhydrogenation, on chromia/K/alumina high temperature dioxygen treatment can remove only a small fraction of the carbon laid down on the catalyst during an experiment. The lower the ratio of total carbon to total hydrogen lost to the catalyst, or the more hydrogen-deficient the carbonaceous overlayer, the easier it is to remove carbon by high temperature dioxygen treatment.

6.5.3 Comparison

Pt/alumina and chromia/K/alumina exhibited some similar properties. On both catalysts dissociation of hydrocarbons results in the formation of a carbonaceous overlayer, containing carbon and hydrogen.

On both catalysts there is isotopic mixing within the carbonaceous overlayer.

The amount of carbon, deposited on the catalyst surface during reactions, which can be removed by high temperature dioxygen treatment is dependent on the ratio of total carbon to total hydrogen lost to the catalyst during a particular experiment. The more hydrogen-deficient the carbonaceous overlayer, the more carbon can be burnt off the catalyst as carbon monoxide or carbon dioxide.

Clearly, in terms of transhydrogenation activity, chromia/K/alumina is a more promising catalyst than Pt/alumina. In order to determine the transhydrogenation activity of Pt/alumina a larger number of hydrocarbon pulses would be required. On Pt/alumina the carbonaceous overlayer eventually blocks the majority of dissociation sites and dehydrogenation should then occur. In theory, if dehydrogenation is possible and hydrogenation is possible, transhydrogenation will occur.

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